PERFORMANCE OF FLUORO-SURFACTANT WITH SUPERCRITICAL CO_2 FLOODING IN HIGH SALINITY CARBONATE RESERVOIRS

BY

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Dedication

I dedicate this effort to my parents, sisters & my nephew.

ACKNOWLEDGMENTS

All praise to the Almighty for his countless blessings bestowed upon me and giving me the strength to complete this work. Without his help nothing is possible. No words of thanks are enough to express my gratitude towards him.

I am proud to have been awarded scholarship by King Fahd University of Petroleum and Minerals throughout my Master's program, for which I am extremely thankful to the University. The journey here will always be a time to cherish for me in the future.

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LIST OF ABBREVIATIONS

CO_2	:	Carbon Dioxide
EOR	:	Enhanced Oil Recovery
IOR	:	Improved Oil Recovery
MENA	:	Middle East and North Africa
PFOA	:	Per-Fluoro-Octanoic Acid
SAGD	:	Steam Assisted Gravity Drainage
BD	:	Barrels per Day
CWI	:	Carbonated Water Injection
IFT	:	Interfacial Tension
SAG	:	Surfactant Alternating Gas
WAGS	:	Water Alternating Gas with Surfactant
AOS	:	Alpha Olephin Sulfonate
MMP	:	Minimum Miscibility Pressure
CT	:	Computerized Tomography
TDS	:	Total Dissolved Solids
PV	:	Pore Volume

ABSTRACT (ENGLISH)

Full Name : Zaid Zaffar Jangda

Thesis Title : Performance of Fluoro-Surfactant with Super Critical CO_2 Flooding in High Salinity Carbonate Reservoirs

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Super-Critical CO_2 flooding combined with surfactants is one of the latest techniques being used for Enhanced Oil Recovery. This overcomes the shortcomings associated with CO_2 gas injection like gravity override and viscous fingering to an appreciable extent and also restricts the mobility of the injected fluid leading to higher contact with the resident crude resulting in better sweep efficiency. Several surfactants have been tested with CO_2 to appraise performance in different scenarios. However there have been problems of surfactant instability at real reservoir conditions of high temperature and high salinity.

In the core-flood experiments performed in this work, an amine oxide-based amphoteric fluoro-surfactant was used for the first time on foot long carbonate cores saturated with high saline formation water. High temperature and pressure was applied coupled with 5 days of aging time with field crude to depict actual reservoir environment. Moreover, three different injection strategies, continuous super-critical CO_2 flooding, alternating injection of super-critical CO_2 and surfactant solution and co-injection of super-critical CO_2 and surfactant solution were performed. All the experiments were conducted on an ingeniously modified coreflooding rig, which was designed to function specifically for this type of experiment.

Results from this core-flood study showed an increase in oil recovery for the novel surfactant-CO_2 system. Interfacial tension experiments were conducted to further judge the role of specifically the surfactant in the increase in oil recovery when it comes in direct contact with oil in high saline environment.

This research aims to provide a new and viable option for CO_2-Surfactant flooding especially for high saline Saudi carbonate reservoirs, showing the usefulness of the surfactant even at very low concentration, thus also mitigating the high cost of this type of surfactants.

ABSTRACT (ARABIC)

ملخص الرسالة

الاسم الكامل: زيد ظفر جانقدا

عنوان الرسالة: دراسة أداء مواد السيرفكتانت الفلورية مع الغمر فوق الحرج باستخدام ثاني اكيد الكربون في المكامن الكربونية عالية الملوحة

التخصص: هندسة البترول

تاريخ الدرجة العلمية: مايو 2014

تعتبر تقنية الغمر فوق الحرج باستخدام ثاني أكسيد الكربون مع مواد السطح الفعالة (السيرفكتانت) احدى اهم الطرق المستخدمة في الاستخلاص المعزز للزيت. من خلال هذه الطريقة يمكن التغلب على بعض عيوب الغمر التقليدي باستخدام ثاني أكسيد الكربون كتأثير الجاذبية واللزوجة إضافة الى ذلك فانه بالإمكان التحكم في حركة سوائل الحقن وهو ما يساعد على توسيع مساحة التلامس مع الزيت المتبقي والذي ينعكس بدوره على فعالية عملية الإزالة. لتصميم مواد سطح فعالة تم دراسة العديد منها ووجد أن أكبر عقبة تتمثل في استقرارية هذه المواد عند درجات الحرارة ومعدلات الملوحة العاليتين.

في هذه الدراسة تم استخدام مواد سطح فعالة امينية اكسجينية القاعدة وذلك في تجارب غمر على عينة كربونية يبلغ طولها قدم واحد مشبعة بمياه طبقات عالية الملوحة. لمحاكاة الظروف المكمنية تم تسليط ضغط وحرارة عاليين على تلك العينة بعد ان تم وضعها في خام زيت لمدة خمس أيام وبعد ذلك تم غمر العينة بثلاث طرق مختلفة، أولها الغمر المستمر باستخدام ثاني أكسيد الكربون فوق الحرج فقط، وفي الطريقة الثانية تم استخدام الحقن المتبادل بين ثاني أكسيد الكربون فوق الحرج ومواد السطح الفعالة، واخيراً تم استخدام الحقن باستخدام ثاني أكسيد الكربون فوق الحرج ومواد السطح الفعالة في آن واحد. تم تطبيق هذه الطرق الثلاث باستخدام نموذج برج حفر مصغر تم تصميمه خصيصا لهذه الدراسة.

أظهرت النتائج المتحصل عليها زيادة في استخلاص الزيت لمنظومة ثاني أكسيد الكربون ومواد السطح الفعالة وللحكم على دور مواد السطح الفعالة في زيادة الاستخلاص تم إجراء تجارب لقياس التوتر السطحي وذلك عند تلامس الزيت مع هذه المواد تحت درجات الحرارة والملوحة العاليتين.

تهدف هذه الدراسة لإيجاد خيارات جديدة وقابلة للتطبيق فيما يتعلق بتقنية الغمر باستخدام ثاني أكسيد الكربون خصوصاً في المكامن الكربونية عالية الملوحة الموجودة في المملكة العربية السعودية والتي يمكن فيها استخدام اقل تركيز من مواد السطح الفعالة وهو ما يساعد على خفض التكلفة العالية لهذه المواد.

CHAPTER 1

INTRODUCTION

As the global energy demand continues to increase and the amount of 'easy' oil diminishes, the world is investing and searching for methods to increase the recovery from the hydrocarbon reservoirs. Additionally, the increasing number of mature fields across Saudi Arabia and the Middle East and North Africa (MENA) region demands new ways of recovering the residual oil. Enhanced Oil Recovery (EOR) is performed to recover the remaining hydrocarbons from a formation that has already produced by primary and sometimes secondary recovery processes. The remaining oil is usually heavy i.e. it has high viscosity which leads to low oil mobility.

A potential EOR solution is through the utilization of CO_2. CO_2 is effective in recovering oil from the reservoir because it promotes swelling of the oil, reduces the viscosity and vaporizes portions of crude oil as it is transported through the porous rock [1]. However as CO_2 is highly mobile, this technique encounters problems of viscous fingering and gravity overriding, as the ability to control the mobility of CO_2 is limited [2]. To overcome this problem, usage of CO_2 with surfactants has been found to be economically and technically viable [2, 3]. Yet the efficiency of this system often decreases sharply during flooding as a result of contact with crude, adsorption of surfactants, high salinity formation water and high reservoir temperature [3, 4]. These issues can be resolved significantly if surfactant formulations are developed which have better tolerance to these factors. Technical

advancements and interest in this area has been rapid and the result is the materialization of a number of surfactant designs that claim to withstand these conditions. This can greatly enhance the utilization of CO_2, cost reduction of surfactant and improvement in oil recovery [5].

Fluorosurfactants have proved to be effective in multiple EOR methods including (i) improving subterranean wetting, (ii) increasing foam stability, and (iii) modifying the surface properties of the reservoir formation [6]. Injection of fluorosurfactant with supercritical CO_2 for improvement of oil recovery should incorporate the advantages of both CO_2 and fluorosurfactant. For the experiments an amphoteric fluorosurfactant was used that had been tested to be stable in high saline environment. It comprised of short chain molecules that do not break into perfluorooctanoic acid (PFOA) which is harmful for the environment [7]. This also diminishes the environmental concern. Moreover, since this surfactant boasts to exhibit excellent performance even at very low concentrations, the cost factor will decrease due to the small amount of surfactant in the surfactant solution. This novel method could prove to be a trendsetter leading to an established technique, applicable in carbonate reservoirs particularly in Saudi Arabia.

This report has been divided into six chapters. Chapter 2 comprises of a literature review of EOR in general and specifically CO_2 and surfactant flooding. Chapter 3 mentions the statement of the problem and the research objectives. Chapter 4 includes the details of the equipment and materials used in the experiments and the detailed procedure of the experiments. Chapter 5 consists of all the results, where they are discussed and compared on the basis of increment in oil recovery and pressure drop response. Chapter 6 gives the conclusions and future recommendations for this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Enhanced Oil Recovery

A considerable percentage of current world oil production comes from mature fields and the rate of replacement of the produced reserves by new discoveries has been declining steadily over the last few decades. To meet the growing need for economical energy throughout the world, the recoverable oil resources in known reservoirs that can be produced economically by applying advanced EOR and Improved Oil Recovery (IOR) technologies will play a substantial part in meeting the energy demands in years to come [8]. EOR processes attempt to increase recovery factor. They focus on the rock/oil/injectant system as well as on the interplay of capillary and viscous forces. On the other hand, IOR refers to any practice used to increase oil recovery. This includes EOR and secondary recovery processes as well as practices to enhance sweep efficiency such as infill drilling, drilling horizontal wells and using polymers for mobility control or improved conformance [9].

CO_2 EOR in the Permian Basin and thermal methods, especially in Canada continue to be the most dominant EOR applications. Cyclic steam injection, steam flooding and SAGD (Steam Assisted Gravity Drainage) have been the most widely used recovery methods of heavy and extra heavy oil production in sandstone reservoirs. Moreover, in-situ

combustion projects have been the second most important recovery method for heavy crude oils in past decades. In carbonate reservoirs, gas injection methods are mostly applied as compared to EOR thermal and chemical methods. N_2 flooding has been an effective recovery process for deep, high-pressure and light oil carbonate reservoirs. However, CO_2 EOR has been successfully implemented in both mature and water flood carbonate reservoirs. Chemical EOR methods, polymer flooding, have shown an increase in pilot tests and few large field implementations including the combination of chemical EOR methods with conformance technologies [8].

2.1.1 Current EOR Practices

Today, the most documented EOR projects are being executed in the US (193 projects), Canada (39 projects), Venezuela (49 projects) and China (39 projects). The volume of oil produced from EOR projects increased significantly from 1.2 MMBD in 1990 to 2.5 MMBD in 2006. US EOR production has increased up to 643 MBD in 2010 representing roughly 14% of total US production [10].

2.1.1.1 Current EOR Practices in the Middle East Region

Middle East is one of the biggest oil producing regions in the world. The International Energy Agency (IEA) estimated that the Middle East provides over 20 MMBD in 2009 representing about one-fourth of the world's total oil production [11]. EOR projects are also receiving attention in the Middle East region and are slowly becoming a strategic target for short and long term production plans (Figure 2.1).

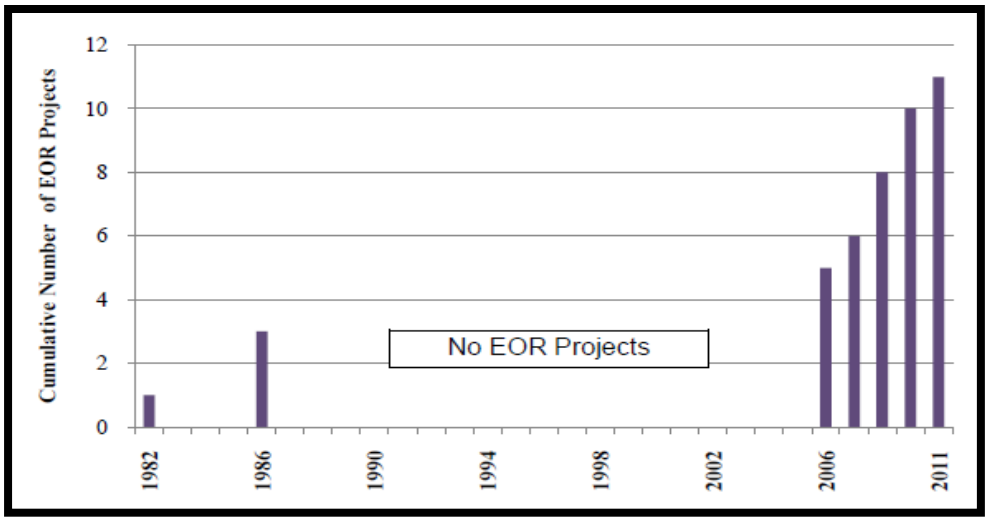


Figure 2.1: Historical Trend of EOR projects in the Middle East region [10]

Currently, there are 11 EOR projects that have been kicked-off either on a pilot scale or commercial scale. Figure 2.2 shows the current status of EOR projects in the Middle East region. Out of the 11 EOR projects, 6 are thermal projects, 3 are CO_2 injection projects, 1 polymer project and one project of water injection with low salinity.

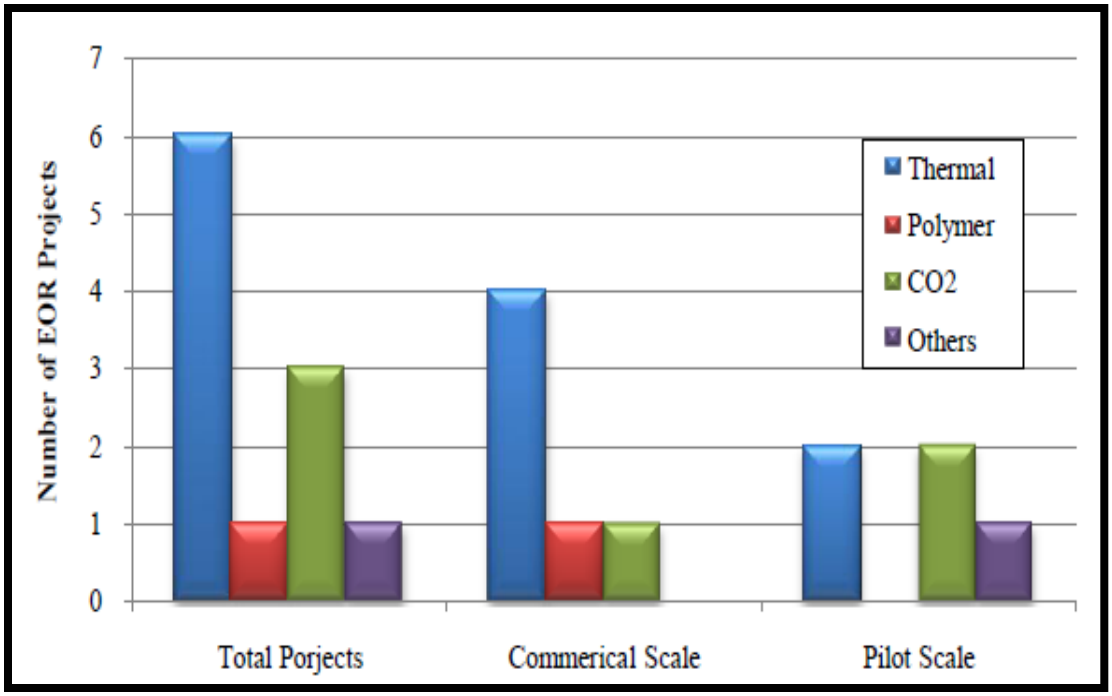


Figure 2.2: Current EOR projects status in the Middle East region [10]

EOR is still not a priority for several coming years in most Middle Eastern countries. However, most ME countries have started to invest in EOR projects because ultimately companies will have to resort to EOR as the "easy oil" gets depleted. There has been a concerted move especially by the ME oil companies to focus on the ultimate oil recovery as compared to immediate oil recovery dictated by short-term profits. This commitment to a long term view will ensure optimum exploitation of the oil resource and maintaining long-term profits. Appropriate EOR methods can then be deployed to maximize ultimate oil recovery.

2.2 CO_2 EOR

CO_2 flooding application in mature fields after primary and secondary recovery over the years has proven to be an important enhanced oil recovery method. Injection of CO_2 at supercritical pressure to displace the immobile oil to producing zone can also serve as a means of reducing the amount of CO_2 in the atmosphere by capturing and sequestering in the mature reservoirs. CO_2 has been closely linked to global climate change hence there are incentives to sequester it. It is a good solvent for light crudes as well as miscible with oil at moderate reservoir pressures. The number of projects injecting CO_2 has been steadily rising and anticipated to increase further in the foreseeable future.

Application of CO_2 flooding as means of enhanced recovery has its challenges which various investigators have tried to solve over the decades. The common challenges being faced are gravity segregation, reservoir heterogeneity and high mobility ratio of CO_2 [12,

13]. These cause a reduction in macroscopic sweep efficiency even though the microscopic efficiency sweep efficiency may be high [14].

CO_2 can easily be in a supercritical fluid state at relatively low temperature and pressure conditions (Critical point at 1070 psi and 32°C). At our experimental conditions (1800 psi and 90°C) CO_2 is a supercritical fluid with a density of 0.3 g/cc and viscosity of 0.025 cp [15].

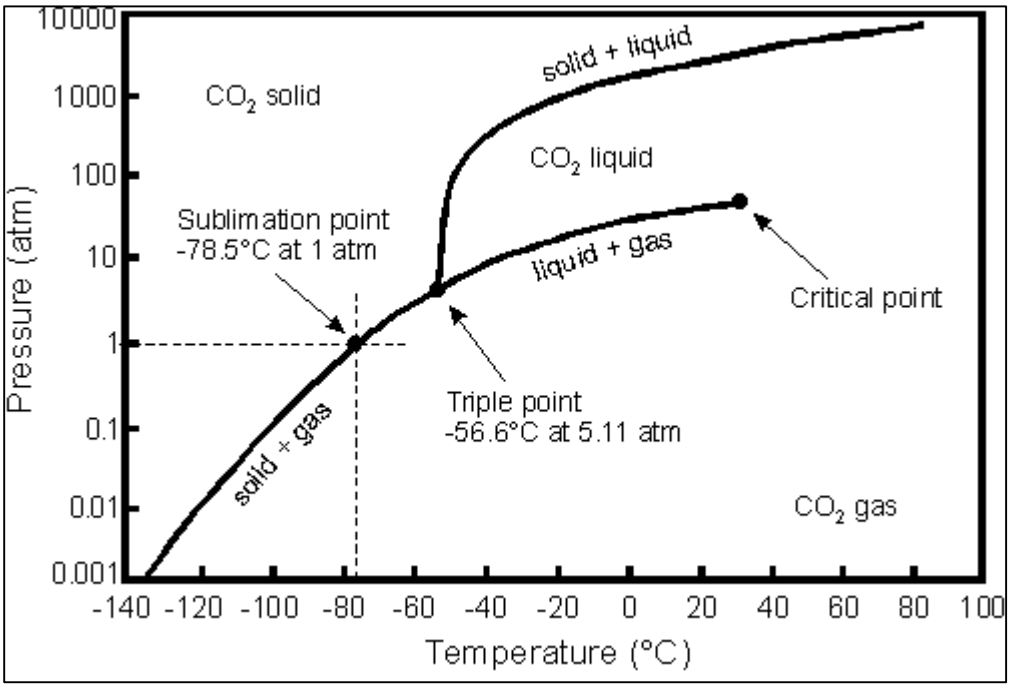


Figure 2.3: Pressure Temperature phase diagram for CO_2

Most of the CO_2 EOR projects focus on the use of supercritical CO_2 especially at higher pressures as it enables miscibility with the oil in the reservoir and achieves higher recoveries. This is due to the fact that supercritical CO_2 has the advantage of high density that is close to liquid density while having a very low viscosity similar to gas viscosity. Therefore, supercritical CO_2 displaces the oil that it contacts effectively but it tends to segregate very quickly reducing the overall volumetric sweep [16]. To alleviate this issue,

strategies have been proposed and developed to inject CO_2 with water, chemicals, viscosifiers and surfactants. Supercritical CO_2 has also been injected along with nanosilica particles to form foam [17]. Core permeability was observed to affect oil recovery in this case in sandstone core plugs. 33 md permeability core showed 13% higher oil recovery than a 270 md permeability core.

Generally, CO_2 has been used in reservoirs containing light oils so that miscibility can be achieved at reservoir pressure. CO_2 is also used in the immiscible mode as it reduces substantially the viscosity of heavy oil, improving the production [18]. Capture and storage of CO_2 remains a big challenge. To reduce global emissions levels it is essential to capture CO_2 from combustion processes. The flue gas emitted from combustion is highly corrosive as it contains oxygen, CO_2 and water and to capture it is technically challenging. However recent advancements have been made in this regard to effectively capture and store CO_2 and also reduce the cost of capture.

2.2.1 Carbonated Water Injection

CO_2 has been also injected as carbonated water to decrease the mobility of CO_2 gas. However the dissolution of CO_2 gas in water as well as high corrosion of the carbonated water remain a hindrance for this method.

The utilization of CO_2 for improving the performance of waterflooding in heavy oil recovery was discussed [19] by presenting the results obtained from an experimental study that consisted of six core flooding experiments (1 consolidated core and 5 unconsolidated sand plugs). They used 2 different injection strategies, which were:

1. Injection of Carbonated Water

2. Injection of 11% and 27% of pore volume CO_2 followed by a soak period and resuming water injection.

The carbonated water used in this experiment was prepared by dissolving CO_2 in 1wt% NaCl brine. Injection of the carbonated water led to recovery of an additional 16.9% Original Oil in Place in the case of consolidated core and 14% in case of sand pack. The size of the carbonated water slug also had an effect on the oil recovery, as higher additional recovery was observed when slug size was increased from 1.5 PV to 4 PV.

Similarly the mechanisms of oil recovery by carbonated water injection were discussed [20] by presenting results of a joint industry research to investigate the performance of Carbonated Water Injection (CWI) as an enhanced oil recovery method.

Using the results of high-pressure direct flow visualization (micromodel) experiments the pore-scale mechanisms of oil recovery by CWI was shown. CWI improved the recovery of both light and heavy oil albeit through different mechanisms. The additional oil recovery in light oil was mainly due to high dissolution of CO_2 in the oil and high oil swelling factor. The viscous oil exhibited a lower swelling factor but a higher viscosity reduction. In both light and viscous oil, CWI recovered more oil compared to conventional water flooding. The carbonated water used in this study was prepared by mixing degassed water with pure CO_2 at 38°C and 2000 psi.

2.3 Classification of surfactants

Surfactants are widely used in oil recovery for particle dispersion, emulsion stabilization, foam generation, reservoir wetting, and many other applications [6]. They are

differentiated basically on the type of charge they possess. For anionic surfactants in solution, the head is negatively charged. This surfactant has excellent cleaning properties and high sudsing potential. However in the presence of calcium and magnesium molecules in the water, the anionic surfactant system suffers from deactivation. The most commonly used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates and soaps. For cationic surfactants in solution, the head is positively charged. Non-ionic surfactants do not have an electrical charge, which makes them resistant to water hardness deactivation. Nonionic surfactants are usually used as co-surfactants and co-solvents to enhance the properties of the primary surfactants. Another type of surfactants are Amphoteric/zwitterionic surfactants. They can be anionic (negatively charged), cationic (positively charged) or non-ionic (no charge) in solution, depending on the acidity or pH of the water. They are compatible with all other classes of surfactants and are soluble and effective in the presence of high concentrations of electrolytes, acids and alkalis. These surfactants may contain two charged groups of different sign. Whereas the positive charge is almost always ammonium, the source of the negative charge may vary (carboxylate, sulphate, sulphonate). These surfactants show high foaming properties [21].

2.4 Surfactants use in EOR

The use of surfactant in foam EOR is to reduce the mobility of the injected fluid by increasing the viscosity which leads to higher sweep efficiency. The capillary forces are reduced due to reduction in interfacial tension by the presence of surfactant [22].

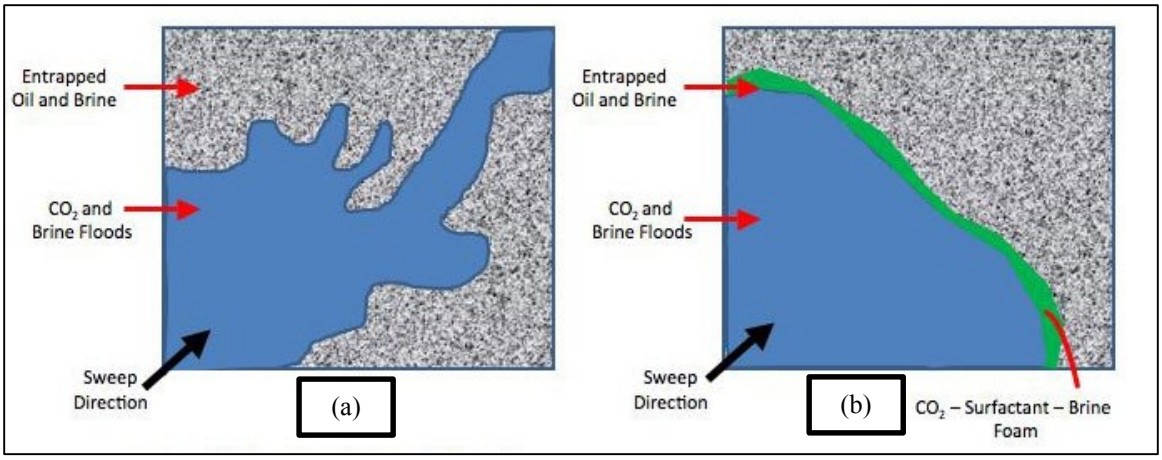


Figure 2.4: (a) Viscous fingering caused by CO_2's high mobility, limiting sweep efficiency, (b) Improved flood viscosity from surfactant, increasing sweep efficiency [23]

Sulfonate surfactants are the common surfactant due to their low adsorption. Different types of surfactants have been synthesized (example is Betaine surfactants which do not require co-surfactants or salts) [24]. Alkyl polyglucoside when in the presence of n-octane show ultra- low interfacial tension and can be used for surfactant flooding [25]. They have low ecotoxicity and have been applied in the fields with high salinities [25]. Alkylphenol ethoxylates use was reduced in the past decade because they are estrogenic. However, a recent modification in their structure renders them non-estrogenic. The change in structure resulted in the formation of alkylphenol alkoxylates, alkylphenol ether sulfate and alkylphenol ether sulfonates. These surfactants give low interfacial tension and are stable within range of salinities, temperature and different oil composition.

Chaser international CD 1045 surfactant has also been used in many investigations. This anionic surfactant has also been found to be effective on carbonate rocks [26] [3] [27]. Alpha olefin sulfonates [22] [28] and DOW chemical's surfactants [29] have also been applied in the field and core floods.

2.4.1 Surfactants for IFT Reduction

Interfacial tension can be defined as the surface tension at the surface of two non-miscible liquids. Oil recovery will increase if the IFT is low as less force will be required for the oil to move. Surfactants are used to lower the interfacial tension between the two fluids (oil and injected fluid), making the oil easier to produce [30]. There are two main methods of measuring IFT of a surfactant-oil system, pendant/rising drop and spinning drop methods. Spinning drop method measures the IFT by rotating a horizontal tube which contains the denser bulk fluid. A drop of a less dense fluid is placed inside the bulk fluid. During rotation the drop elongates until the interfacial tension and the centrifugal forces are balanced, at which point the IFT is measured. This method is mostly used for measuring very low IFT values. Pendant or rising drop method is used for relatively high IFT measurements. A drop of liquid is suspended in the bulk fluid from the end of a capillary by surface tension. The shape of the drop is determined by the balance of interfacial tension and gravity force. The interfacial tension is then measured by the drop shape and the densities of the two fluids. Surfactant concentration effect on IFT was studied [30] for two surfactant systems with oil and it was observed that the IFT decreased as the concentration of surfactant increased for both the systems.

2.5 Fluoro surfactants in EOR

The use of fluorosurfactants is a recent but growing trend due to (i) the exceptional hydrophobic and oleophobic nature of the perfluoroalkyl and perfluoroalkyl ether groups, (ii) the effectiveness of fluorosurfactants at extremely low concentrations, and (iii) the

availability of anionic, cationic, nonionic, and amphoteric fluorosurfactants which can modify surfaces and interfaces better than conventional hydrocarbon surfactants [6]. The bond strength of the carbon-fluorine bond in perfluoroalkyl and perfluoroalkyl ether groups has been demonstrated as the key to remarkable overall stability for fluorochemicals and fluoropolymers. Fluorosurfactants possess a combination of excellent chemical and thermal stability, and wetting ability [6]. For foam injection EOR, fluorosurfactants have the unique benefit to stabilize foam that is in contact with the crude oil, while imbibing and transporting the oil through the subterranean formation [6].

2.6 Surfactants use in CO_2 EOR

Bernard and Holm gained the first patent for use of foam to control the mobility of CO_2. Surfactants have been used to control the mobility of CO_2. Surfactant- CO_2 flooding has its own challenges which has been the focus of research at the laboratory core flood and field scale simulation using various commercial simulators like CMG-STARS [31] [27] [29]. Various attempts have been made to investigate the factors that influence surfactant-CO_2 flooding. Partitioning between CO_2 and water phases is more sensitive to surfactant structure than temperature and pressure. Strong foam is observed for non-ionic surfactants and increasing the partition coefficient reduces foam propagation [27]. High crude oil presence can cause destabilizing effects on the CO_2 foam and can be used as selective plugging for high water cut zones [32]. This has been confirmed experimentally, when the foam is injected above its MMP there was considerable oil recovery but when injected below MMP no extra production of oil is noticed [22].

Injection strategy is another important factor considered when flooding CO_2 surfactant foams. Le et al [29] came up with novel injection strategy which resulted in the reduction of loss of surfactant, cost due to adsorption of surfactant loss and improved the in-situ foam generation. Identification of cost effective, environmentally friendly materials that dissolve in super-critical CO_2 for use in EOR has been the subject of extensive research. Supercritical CO_2-philes (materials soluble in super-critical CO_2) are rare and use of these materials as surfactants was not possible due to the high pressures required to dissolve them (a result of their high molecular weight) and the inability to cost-effectively add a hydrophilic group for solubility in the bulk recovery fluid (water) [33]. Lately however, these surfactants have been introduced. The surfactant produced by DOW Chemicals was dissolved in CO_2 that resulted in a higher recovery without injected water. Experimental and simulated field result were consistent, indicating higher recovery as compared with the conventional method of CO_2 injection.

Chaser international CD 1045 surfactant has been tested in sandstone cores [32] at reservoir pressure and temperature conditions. It was observed that CO_2 foam had higher oil recovery than CO_2-brine co-injection.

Ethoxylated cocoamine surfactants have been tested [34] by injecting them along with CO_2 in sandpacks at 120°C and at high salinity for stable CO_2 foam. These surfactants have high cloud points and are soluble in CO_2. The stability depends upon the variation in the tail length and degree of ethoxylation. These surfactants have also shown decreased adsorption on carbonate rock material.

Few surfactants have been developed that can dissolve in supercritical CO_2 at relatively mild conditions. The fluorination is not an essential requirement for solubility, but the most effective surfactants in supercritical-CO_2 often contain partially fluorinated or fully fluorinated chains [35]. Enick and his group [36] evaluated a number of CO_2 thickeners that incorporated fluorocarbon chains. They established through viscometry and coreflood tests that a copolymer having a composition of 29 mol% styrene and 71% fluoroacrylate exhibited remarkably high solubility in dense CO_2, drastically increased the viscosity and reduced the mobility of CO_2. The same group recently conducted [37] foam stability tests using a number of commercially available surfactants of four different categories namely branched alkylphenol ethoxylates, branched alkyl ethoxylates, fatty-acid-based surfactants and predominantly unbranched alkyl ethoxylates. They found out that a many of the available, water-soluble, nonionic surfactants can dissolve in CO_2 and also stabilize CO_2-in-brine foams in situ. This has provided the option of introducing surfactant directly into the CO_2 phase while flooding.

However to the best of our knowledge, there has been no reported work of thermal stability of fluorinated surfactants and its role in increasing recovery with supercritical CO_2 for EOR application.

2.6.1 Factors Affecting Surfactant CO_2 Flooding

The injectivity of surfactant has been the focus of various researches. Various injection strategies have been tried. Surfactant alternating gas (SAG) method with surfactant dissolved in water is one of them. Increasing injectivity with this method causes a reduction in gravity segregation in cases where injection pressure is constrained [38]. Multiple smaller slugs of a surfactant and CO_2 were found to enhance foamability and stability

compared to large alternating slugs [39]. Co-injection is another way of injection. Surfactant and CO_2 co-injection produced better foam than SAG [31]. Le et al [29], came out with two new novel approach of injection. Novel WAGS, water alternating gas with surfactant dissolved in CO_2 and novel CO_2 (i.e. continuous CO_2 injection with dissolved surfactants). Soluble CO_2 surfactants could cause a delay in propagation of foam enhancing foam robustness [27].

A critical factor to consider is the adsorption of surfactant onto rock surface due to its amphipathic nature [40]. Main factors affecting the adsorption of surfactant onto rock surface are; surfactant nature, temperature, salinity and hardness, rock type, wettability and presence of residual oil [41]. Residual oil presence increased the adsorption of CD 1045 by about 32% [31]. To satisfy the requirement for permanent adsorption, additional amount of surfactants are needed for CO_2-foam propagation [40]. Prolonged injection of surfactant may lead to adsorption to the rock and will not contribute to the formation of foam [39]. Adsorption of surfactant was found to be lower in high temperature formations [42]. Co-surfactants system has been suggested as a means of reducing the amount of expensive surfactants and replacing it with less expensive ones [43]. It was observed from laboratory core floods that the foaming agent could be reduced by at least 75% and injectivity as much as 50%. An increment in surfactant partitioning coefficient reduced the rate of foam propagation [27]. The mobility of foam is affected by quality of foam [44]. A decrease in foam mobility was observed with increasing foam quality between ranges of 33.3% to 80%. A number of studies have shown that when the foam quality is between 45% and 95%, foam exhibits good mobility reduction.

The effects of salinity, pressure, surfactant concentration, foam quality adsorption, and oil effects on supercritical CO_2 foam in Berea sandstone cores were evaluated [5]. A number of surfactant formulations; AOS, Betaine and their mixtures, were compared and analyzed based on a systematic screening process. The experimental results concluded that these surfactant mixtures make the CO_2 foam more resistant to crude oil and less adsorption on sandstone compared to individual Betaine. Total oil recovery for the miscible flooding increased in both heterogeneous and homogenous samples compared to immiscible flooding.

A strong correlation between CO_2 density on the foam strength was observed [15] by co-injecting sc-CO_2 and AOS surfactant in Berea sandstone cores. At low CO_2 density, moderate to strong foams were generated for both gaseous and sc-CO_2, while weak foams were observed where the density of the sc-CO_2 was larger than 0.5 g/cc. Permeability is the most important rock property that affects foam propagation. Experiments indicate that foam reduces gas mobility more in high permeability porous media than in low permeability media [45].

2.7 Visual Experiments

Surfactant was co-injected with CO_2 gas and also with supercritical CO_2 in glass micromodels [46] and foam was observed at ambient conditions. At high temperature and pressure and in the presence of oil, initially instead of foam formation, an emulsion was formed and oil was displaced rapidly from the outlet. Foam was formed after the saturation of oil declined.

CO_2 and N_2 foams were compared [47] to observe the increase in oil recovery for extra-heavy crude oil. Neodol surfactant (0.3 % wt.) was injected with CO_2 and N_2 as gaseous phase in different experiments in a high pressure glass micromodel. N_2 foam was more stable than CO_2 foam but was less efficient in recovering the heavy viscous oil as CO_2 foam recovered 60% more oil. The superior performance of the CO_2 foam was due to the significant reduction in oil viscosity. Foam was also able to gradually spread in the low permeability zones, leading to recovery of the residual oil from those regions of the micromodel.

Visual observation by means of a sight glass installed at the core outlet also showed coarser CO_2 foams in contrast to denser N_2 foams as a result of co-injection with AOS surfactant in Berea cores [15].

CHAPTER 3

PROBLEM STATEMENT AND RESEARCH OBJECTIVES

As evident from the literature, a concentrated effort is being done worldwide to develop a surfactant-CO_2 system that works in actual reservoir conditions. However, most of the work done till now has deficiencies that restrict their applicability. The majority of surfactants used in earlier works have not been tested in high saline environment usually encountered in Saudi reservoirs. Inability of foam generation and instability of foam means that the problem of high mobility of CO_2 is not tackled, ceasing all the benefits thought to be associated with a quality foam system. Adsorption of the surfactant on the rock material is another factor which reduces the effectiveness of the foam system. Moreover, very limited foam experiments have been conducted on carbonate rocks and even less so on long cores. Thus an investigation into the synergistic properties of a surfactant-CO_2 formulation is proposed as a possible solution to this problem.

In this work, a fluoro-surfactant was used with CO_2 that has been tested in high saline environment and is designed to work in high temperature conditions. Foot long carbonate cores were used in our research to see the full effect of the injected fluid as it propagates through the core. Another uniqueness will be a sufficiently longer aging time of the core

with oil in an attempt to depict real reservoir conditions. All the experiments will be conducted at pressures that are routinely found in real reservoirs.

The main goal of the thesis is to evaluate sc-CO_2/Fluorosurfactant as an EOR solution applicable to Saudi Reservoirs. The objective here is to carry out core-flooding experiments to study oil recovery from limestone rock using sc-CO_2/Fluorosurfactant system and to determine the optimum injection strategy. Additionally Interfacial Tension tests were planned to specifically ascertain the role of the surfactant in the increment of oil recovery.

CHAPTER 4

EXPERIMENTAL PROCEDURE AND METHODOLOGY

For our research, an experimental core-flood setup was used to conduct flow through the prepared core samples. The set-up is composed of fluid injection pumps, fluid accumulators, absolute and differential pressure transducers, temperature transducer, core holder, back pressure regulator, overburden pressure pump, pressure multiplier, data acquisition system and an oven. Control and safety valves, tubing, and fittings are integral part of the setup. This equipment was used in conducting tests to determine the efficiency of the CO_2-surfactant system in improving oil recovery. The flooding system was integrated with a data acquisition system to record all data generated during the flooding test. A brief description of all the materials and the equipment as well as the detailed procedure followed in the experiments is described below.

4.1 Materials

4.1.1 Core Samples

Indiana Limestone cores of 12" length and 1.5" diameter were used in all the experiments. The core samples were procured form Kocurek Industries (USA). The supplier specified porosity and permeability values were 19 % and 70 md respectively.

4.1.2 Salts

Five different salts were needed to prepare both the synthetic formation and injection brines. These salts were Sodium Chloride (NaCl), Sodium Hydroxide (NaOH), Sodium carbonate (Na_2CO_3), Calcium Chloride ($CaCl_2$) and Magnesium Chloride ($MgCl_2$). These salts are shown in Figure 4.1.

Figure 4.1: Salts used for brine preparation

4.1.3 Brines

Two types of brines were required for the experiments. Formation brine to saturate the core initially and injection brine for water-flooding. The concentrations of the brines resemble Saudi reservoir connate water and sea-water for saturation and injection respectively. The brines were stirred and heated for 48 hours prior to usage in the experiments. Table 4.1 shows the concentration of the two brine solutions.

Table 4.1: Brine Concentrations

Brine Concentrations (ppm)		
Ions	**Connate Water**	**Sea Water**
Sodium	59,491	18,300
Calcium	19,040	650
Magnesium	2,439	2,110
Sulfate	350	4,290
Bicarbonate	354	120
TDS	**213,734**	**57,670**

4.1.4 Oil

Uthmaniya Dead Oil (Saudi Crude) was used in the core-flooding experiments. The oil was filtered using 7 micron filter before using it for the experiments. The API gravity of the oil was 30.1° at room conditions, while the viscosity which is a function of temperature, followed the trend shown in Figure 4.2.

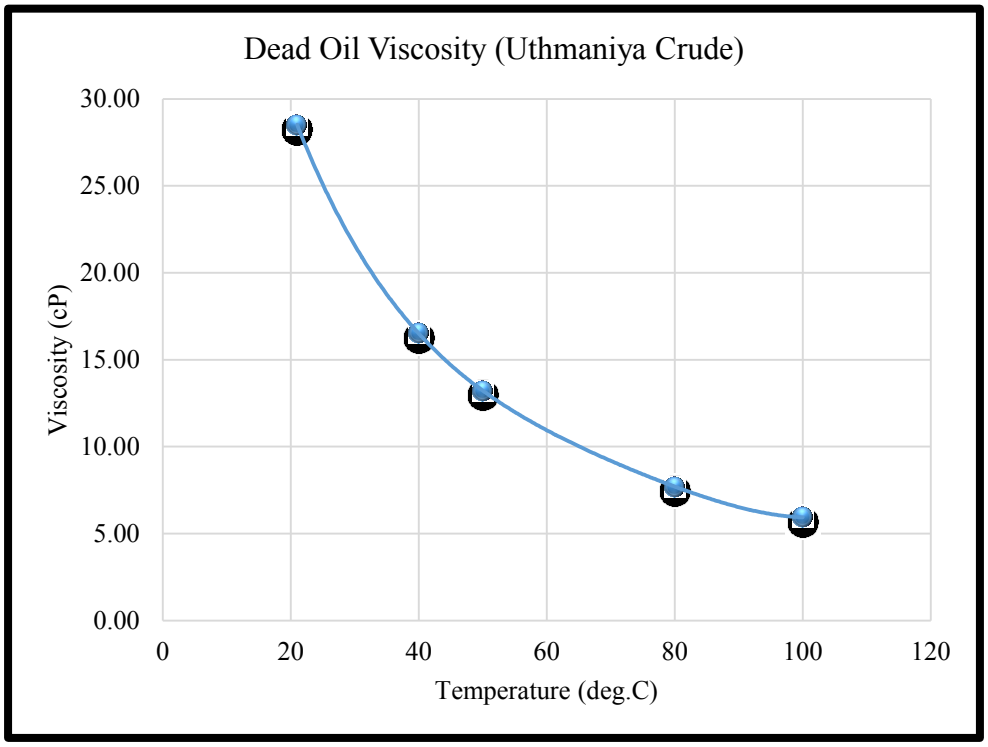


Figure 4.2: Oil viscosity measurements

4.1.5 Surfactants

The amphoteric amine oxide-based fluoro-surfactant was supplied by DuPont in ample quantity for the various experiments. The non-fluorinated surfactant which was used in the last experiment for comparison was a hydrocarbon surfactant (Ethomeen). The surfactant solutions was prepared by adding surfactant at a concentration of 0.15% (vol.) in the injection brine.

4.1.6 CO_2

Industrial Grade CO_2 was obtained in sufficient quantity in the form of gas cylinders. The CO_2 was then transferred into the cells in the core flooding system.

4.1.7 Toluene

Toluene was used to clean the entire system before each experiment. Being a good solvent of oil it provided good cleaning of all the lines containing any traces of oil.

4.2 Equipment

4.2.1 Core-flooding experimental setup

The core-flooding system used in this study is basically a reservoir condition condensate depletion system that was modified to suit the required specifications. The schematic of the core-flooding experimental system is shown in Figure 4.3. The system consists of an oven, five floating piston fluid cylinders of various volumes, Quizix pumping system, back pressure regulator and the core holder. The components of the flow, control and measurement systems are installed on the ends of the oven, on its roof, as well as within

the oven itself. The system includes 72 air operated solenoid valves that are controlled by a software on a dedicated computer. The flow control system components are all inside the oven. All the pressure transducers and Quizix pump controllers are external to the oven. The system is hooked up to an automatic data logging system which works with the software to record all the data during the experiments in a Microsoft Excel© workbook.

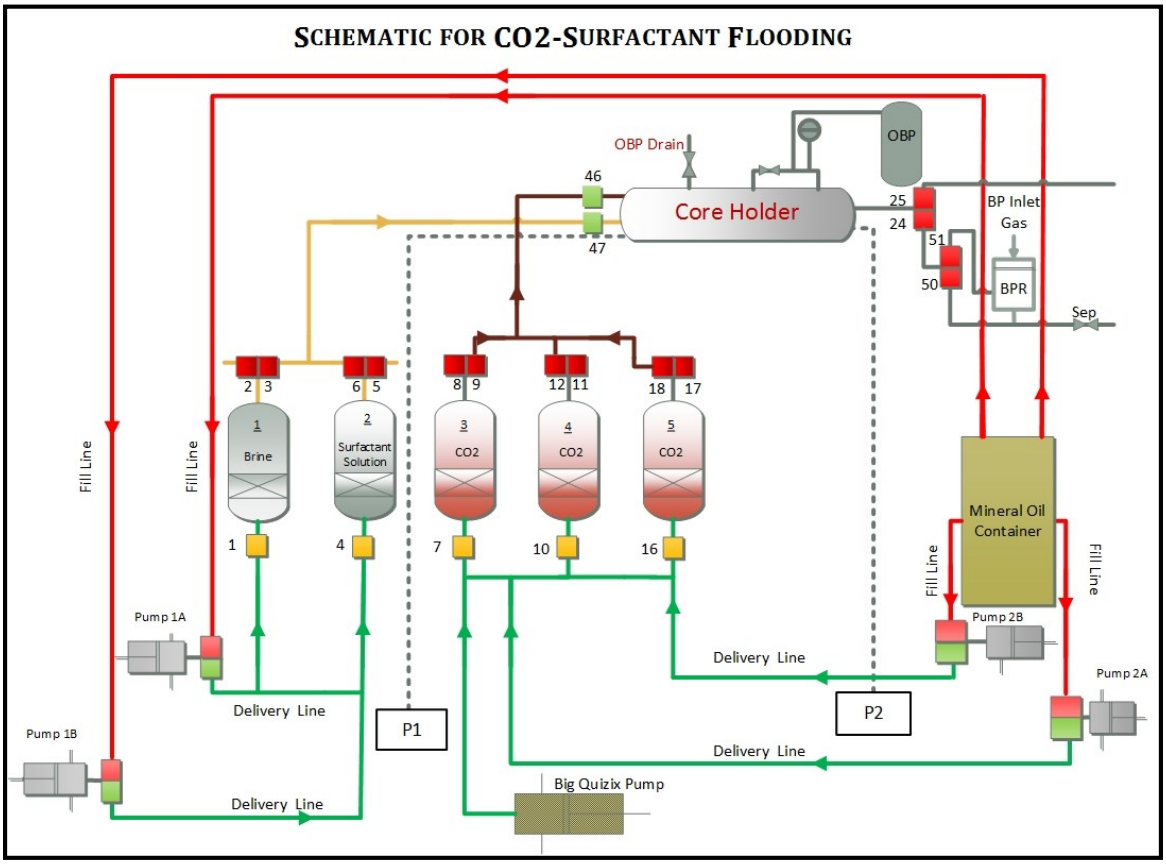


Figure 4.3: Schematic of the core-flooding experimental setup

A brief description of the main components of the system is given below

4.2.2 Pumps

4.2.2.1 Quizix Pumping System

The pumping system is made up of six computer controlled positive displacement Quizix pumps. These are very robust precision pumps and are capable of injecting fluids at high temperature and pressure into the core at various predetermined flow rates. Each pump has a separate cylinder, since two pump cylinders are required for continuous flow. The pump cylinders are controlled by a controller for automatic operation. Normally, one cylinder injects fluid into the core while the other is charged or filled through a return line. The system is purposely designed in such a way that the receiving cylinder operates at a slightly higher rate than the delivering cylinder. The objective is that the receiving cylinder is ready to take over to inject fluid into the core prior to the emptying of the delivering cylinder. The pumping system can be used in 3 or 5 pump recirculation modes. In a 3 pump mode, two pumps are used for delivering fluids (liquid and gas) into the core while the third pump acts as a servo pump or back pressure regulator to maintain desired pressure in the system. In a 5-pump recirculation mode, four pumps are used for delivering fluids (liquid and gas) into the core while the fifth pump acts as a servo pump. The sixth pump is employed as a standby pump, which can be used in case of the failure of the fifth pump. The Quzix pumping system is placed in the oven to maintain reservoir conditions of temperature and pressure. The Quzix pumping system window displays all the pumps with operating parameters such as pressures and flow rates, and the user can change these parameters whenever required.

4.2.2.2 Overburden Pressure (OBP) Pump:

A high-pressure syringe pump (ISCO 100D) was used to apply and maintain required overburden pressure (OBP) on the core holder.

4.2.2.3 External Pumps

Two pumps were used externally in the core flooding experiments. An Eldex pump was used to inject formation brine to build up the pressure and a positive displacement ISCO pump to inject oil in to the core to displace the formation water and saturate the core with oil.

4.2.3 Auxiliary Accessories

Five high-pressure transfer cells of various volumes were incorporated in the experimental setup to store and inject the fluids. Two of them were one liter cells to contain the injection brine and the surfactant solution, while the other three cells (two 2 liter cells and one 3 liter cell) all contained CO_2. All the cells were located inside the oven to main desired temperature of fluids. Another high pressure titanium cell acquired through Vinci Technologies was connected to the system by an external valve. This cell contained the oil to be injected into the core through the ISCO pump. The differential pressure across the core was measured using two differential pressure transducers, one was low range (50 psig) and the other was high range (500 psig). These transducers have high resolution and automatically switch from low to high during the experiment depending on the differential pressure developed in the core. The inlet and outlet core pressures are monitored by precision Quartzdyne pressure transducers that give accurate absolute pressure. During the experiment the core was fitted in to a stainless steel hassler type core holder manufactured

by Core Laboratories. It could accommodate up to 2 ft. long core and the maximum working pressure of the core holder was 7500 psig.

4.2.4 Back Pressure Regulator:

A dome shaped back pressure regulator was employed to apply and control the back pressure. Nitrogen was used as a medium for back pressure application.

4.2.5 Computerized Tomography (CT) Scanner.

Toshiba Medical CT Scanner (Figure 4.4) was used to perform CT scans of the cores. It could generate CT data for the cores with a minimum slice thickness of 1 mm.

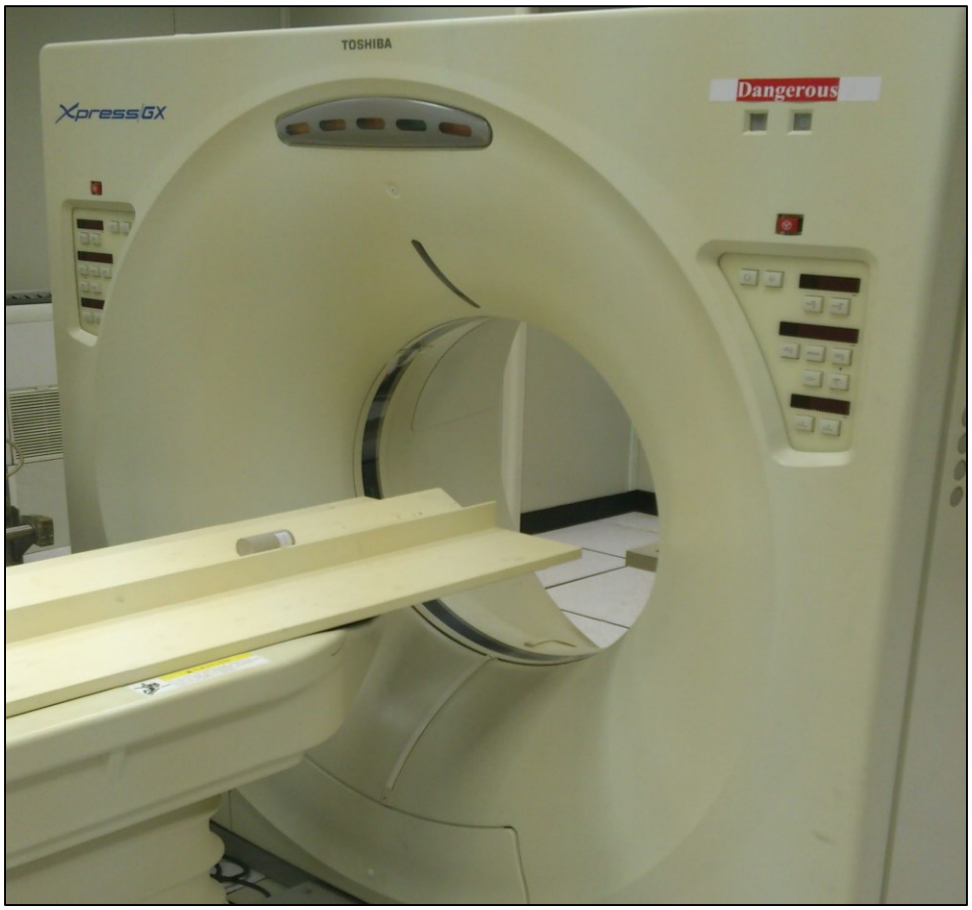


Figure 4.4: Toshiba Medical CT Scanner

4.2.6 Digital Height Gauge

To measure the core dimensions, a digital height gauge (Mitutoyo 192-605) was used. This gauge provided accurate length and diameter measurements of the cores and is shown in Figure 4.5.

Figure 4.5: Mitutoyo Digital Depth Gauge

4.2.7 Analytical Weight Balance

A high accuracy analytical weight balance (Sartorius Cubis® Precision Balance MSE5203S-000-DE) was used to measure the weight of the cores, both dry and wet, and also for the measurements of the salts during brine preparation. The balance is shown in Figure 4.6.

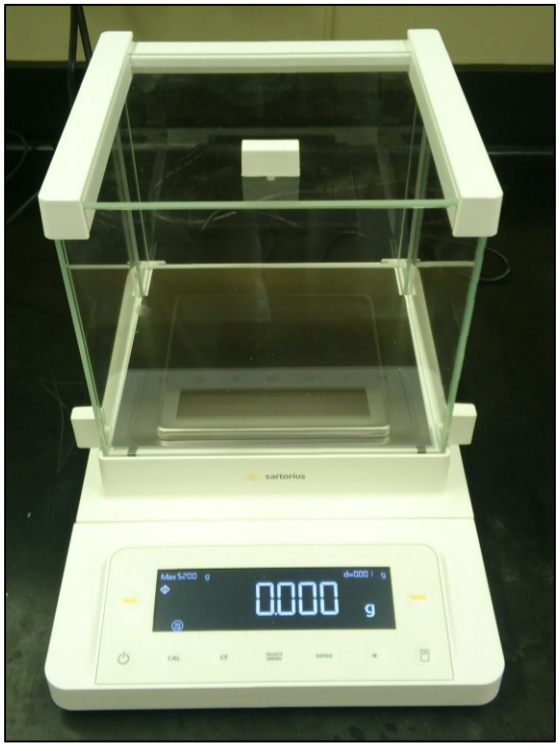


Figure 4.6: Sartorius Cubis® Precision Balance

4.2.8 IFT Equipment

The interfacial tension between the injected brine and oil and the surfactant solution and oil was measured using IFT 700 equipment manufactured by Vinci Technologies (Figure 4.7). This machine was designed to perform experiments at high pressure (up to 10000 psi) and high temperature (up to 200°C) and could measure IFT values between 0.1 to 72 mN/m. A drop of oil was created from a calibrated capillary into the bulk fluid (injection

brine or surfactant solution) at our experimental conditions, in a viewing chamber which had a capacity of 20 cc. Then, using rising drop method (since the density of oil was less than each of the bulk fluids), a camera connected to the computer recorded the shape of the drop and solved the Laplace equation to provide the interfacial tension values. The accessories equipped with the main equipment were two manual pumps for the sample fluids (bulk and drop fluids), Peltier Thermostat (PT100) temperature sensor, electric heater, a control panel with a temperature regulator, which enables to set the temperature of the system and one pressure indicator. The video system to view the drop and display it on the computer screen consisted of a CCD color camera 1.4MPixel, a macro zoom lens and an LED for lighting. A computer with the software installed was connected to the system to display and save the results.

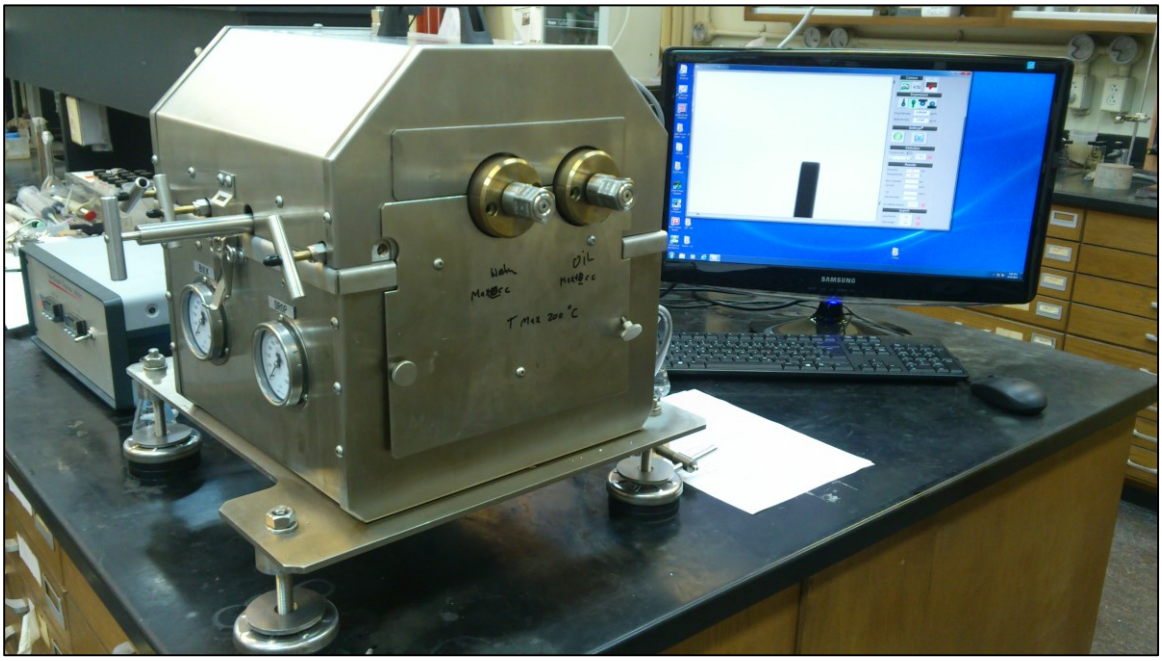


Figure 4.7: Vinci Technologies IFT 700

4.2.9 Density meter

In order to measure the IFT, the density of the fluids at the desired condition is required. These values were obtained using the High Pressure Density meter (DMA HP) manufactured by Anton Paar (Figure 4.8). This equipment was designed to measure the density of liquids and gases under high pressures (up to 10,000 psi) and high temperatures (up to 200°C). In order to get these measurements the DMA HP cell formed one part of the complete setup. This setup had to be adopted to the particular requirements of each individual application. Temperature control of the DMA HP was carried with an integrated Peltier thermostat. To display the measuring parameters, DMA HP was connected to a master instrument (DMA 4500). The density is measured based on the oscillating U-tube method. The DMA HP measures the period of harmonic oscillation of the built-in U-tube which contains the sample. The period of oscillation is converted into the density of the filled-in sample by the master instrument (DMA 4500).

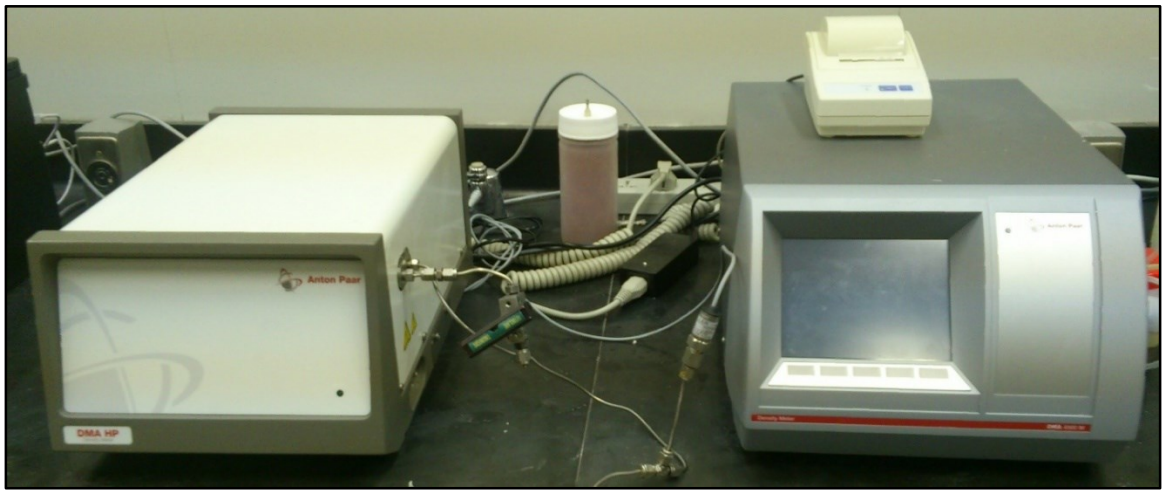


Figure 4.8: Anton Paar DMA HP and DMA 4500

4.3 Methodology

4.3.1 Experimental Plan

A number of experiments were planned in which the parameters were varied to accommodate the effect of various factors on the increase in oil recovery. Three injection strategies were considered:

1. CO_2 Flooding- base case.
2. Alternate Surfactant and CO_2 Flooding- slugs of different ratios of surfactant solution and CO_2 were injected alternatively in subsequent experiments.
3. Continuous Surfactant and CO_2 Flooding: Surfactant solution and CO_2 was injected simultaneously.

The experiments were designed to depict reservoir conditions, thus some of the parameters were kept constant. These include:

- Temperature: 90°C
- Pressure:
    - 2500 psi (overburden pressure)
    - 1800 psi (backpressure)
- Crude Oil: Uthmaniya dead oil (30.1°API)
- Core: Indiana Limestone 12” x 1.5”.
- Brine Salinity:
    - Connate Water = 213,734 TDS
    - Injection Brine = 57,670 TDS

- Oil Soak Period: 5 days (aging time)
- Injection Flow Rates:
    - Oil: 0.25 cc/min
    - Water: 0.5 cc/min
    - Surfactant solution: 0.3 cc/min
    - CO_2: 0.3 cc/min
    - Co-injection:
        - Surfactant solution: 0.15 cc/min
        - CO_2: 0.15 cc/min
- Surfactant Concentration: 0.15 % (vol.)

The parameters that were varied to find the optimum strategy were:

- Surfactant Type
    - Fluoro-Surfactant.
    - Ethomeen surfactant (hydrocarbon).
- Injection Volume (slug size):
    - Equal Surfactant solution and CO_2 slugs (2.5 PV).
    - Smaller surfactant solution, larger CO_2 slugs (2.5 PV).
    - Larger surfactant solution, smaller CO_2 slugs (2.5 PV).
    - Surfactant + CO_2 (2.5 PV)

4.3.2 Core-flooding Experimental Procedure

To carry out the experiments a detailed procedure was devised which is detailed as under:

4.3.2.1 Measurement of Core Properties

Firstly, core dimensions were measured, i.e. dry weight, length, diameter and bulk volume. These measurements were required for the bulk volume, pore volume and porosity calculations.

4.3.2.2 Core Saturation

Core was then evacuated and saturated with synthetic formation brine in a high pressure cell at 1800 psi for up to 48 hours

4.3.2.3 CT Scan of Cores

For some of the experiments the cores were CT scanned both before and after saturation with the connate water. The CT numbers obtained were used to estimate porosity using the formula [48]:

$$Ø = \frac{CT_{wet} - CT_{dry}}{CT_{water} - CT_{air}} \quad (4.1)$$

Where,

CT_{wet} = Mean CTN of the slice with core saturated with water, HU
CT_{dry} = Mean CT number of the slice when the core is dry, HU
CT_{water} = Mean CT number of the water, HU
CT_{air} = Mean CT number of air, HU

4.3.2.4 Core Loading

The core was then loaded in the core-holder and then pressure tested by an external pump by applying an overburden pressure of 1000 psi for up to 24 hours. After making sure that there is no leakage or pressure drop the core holder was fitted into the oven.

4.3.2.5 Pressure Build-up and Re-saturation

1 Pore Volume (PV) formation brine was then flowed through the core to completely re-saturate the core and build the pressure up to the required reservoir pressure i.e. 1800 psi. Overburden pressure was increased simultaneously to 2500 psi to maintain a net 700 psi pressure differential. Backpressure was applied using nitrogen gas to control the pore pressure.

4.3.2.6 Oil Saturation

1.5 PV oil was then injected at 0.25 cc/min to saturate the core and get Initial Water Saturation (Sw_i), which was measured by simple material balance keeping track of the injected and produced fluids.

4.3.2.7 Heating of the system and aging

The oven was then started to heat the system gradually to 90°C. The core was then left to age at that temperature for 5 days.

4.3.2.8 Water Flooding

Waterflooding was performed after aging of the core, by injecting the prepared injection brine at 0.5 cc/min till 2 PV of the system. Oil recovery was calculated by measuring the produced oil from the core.

4.3.2.9 CO_2-surfactant flooding

Brine flooding was followed by the different injection strategies that were designed and are described in the Table 4.2.

Table 4.2: Injection strategies for the core-flooding experiments

Base Case	**Experiment 1**	CO_2 Flooding	2.5 PV CO_2
Alternate Surfactant Solution-CO_2 Flooding	**Experiment 2**	Equal Slug Sizes (Total 2.5 PV)	1. 0.5 PV Surfactant Solution 2. 0.5 PV CO_2 3. 0.5 PV Surfactant Solution 4. 0.5 PV CO_2 5. 0.25 PV Surfactant Solution 6. 0.25 PV CO_2
	Experiment 3	Smaller Surfactant Solution, Larger CO_2 slugs (Total 2.5 PV)	1. 0.25 PV Surfactant Solution 2. 0.75 PV CO2 3. 0.25 PV Surfactant Solution 4. 0.75 PV CO2 5. 0.125 PV Surfactant Solution 6. 0.375 PV CO2
	Experiment 4	Larger surfactant solution, smaller CO_2 slugs (Total 2.5 PV)	1. 0.75 PV Surfactant Solution 2. 0.25 PV CO2 3. 0.75 PV Surfactant Solution 4. 0.25 PV CO2 5. 0.375 PV Surfactant Solution 6. 0.125 PV CO2
Simultaneous Surfactant Solution-CO_2 Flooding	**Experiment 5 and 6**	Co-injection (Total 2.5 PV)	2.5 PV Surfactant Solution + CO_2

The CO_2 and the surfactant solution were injected at 0.3 cc/min during the individual and alternating experiments and at 0.15 cc/min during the co-injection experiments. The increase in the oil recovery through each method or strategy was noted and then compared at the end to propose the best technique observed. All the flooding schemes were followed up with another brine cycle to thoroughly displace all the movable oil from the core.

The oven was then switched off, pressure was released and the core removed from the system for CT scan. Cleaning of the system was done after each experiment in preparation for the next experiment.

4.3.3 Interfacial Tension Measurements

4.3.3.1 Density Calculations

In order to perform the IFT experiments, firstly the density of the fluids was measured at the desired experimental conditions (90°C and different pressures). This was done using the high pressure density meter described earlier. Firstly, before making any measurements the equipment was calibrated with two fluids of known density at each of the desired conditions. Nitrogen gas and distilled water were used as the reference fluids. Each of these fluids were injected into the cell at the desired temperature (90°C) and each of the pressure conditions. The temperature was set using the heater and the two thermostats present inside the cell and the pressure was kept constant using an ISCO syringe pump. The density values were input into the software based on which two coefficients were calculated and the density adjusted for that particular condition. Once the equipment was adjusted for each point, the samples for which the IFT had to be calculated were introduced into the cell and the density values were measured according to the density adjustment at that condition.

4.3.3.2 IFT Procedure

The main steps for the calculation of the IFT using the IFT 700 equipment are detailed below:

1. All the lines, viewing chamber, transfer cells and the capillary were cleaned and dried before being fitted into the main steel base of the equipment.
2. Vacuum was then applied to evacuate the cells, chamber and the lines of any air.
3. The desired working temperature was set.
4. The drop and bulk fluids were then loaded
5. Then the desired pressure was set using the manual pumps.
6. The experiment to be conducted was defined on the software (rising drop for our case).
7. The drop and the bilk density values calculated earlier were entered.
8. Camera focus was then performed to get a clear view of the chamber.
9. Calibration of the needle was done and the detection lines were adjusted.
10. The export parameters were defined to save the results and the images on the computer.
11. The drop of oil was then created.
12. Depending on the drop, the detection level was adjusted and then the measurements were started and the results and images were saved. In addition to the IFT value, the software also measured the drop diameter, drop volume and the bond number.

Only those results were used and reported where the drop of oil was stable for at least 10 minutes. The software developed for this equipment takes into account all the points from the shape of the drop to solve the Laplace equation to calculate the IFT. The software uses

at least 80 points on the shape of the drop for the IFT calculation. This enables increased accuracy as earlier software only used two or three main parameters to compute the IFT.

CHAPTER 5

RESULTS AND DISCUSSION

Specifically designed coreflooding experiments were performed in this research to help understand the complex phenomena occurring in a hydrocarbon reservoir as a result of rock and fluid interaction in the harsh subsurface conditions. Coreflooding experiments provide the nearest depiction of an actual reservoir that can be achieved on the lab scale. The actual environment present under thousands of feet of rock is created as part of a process that has been going on for millions of years. This, can never be obtained in the laboratory. However, the equipment and resources available allowed the design of the experiments at conditions that can be stated as 'similar' to an actual reservoir. Thus the results can be up-scaled and with the help of proper simulation, a real field performance can be predicted.

The coreflooding experiments conducted in this study followed a step-by-step procedure that has been briefly explained earlier. The results of each step are described in the sections below.

5.1 Core-flooding Experiment Results

5.1.1 Measurement of core dimensions

The dimensions of each core were measured before starting the experiment. The core diameter, length and weight were measured to calculate the bulk volume of the cylindrical core. The core weight was again measured after brine saturation. The difference in weight between the wet and the dry core was divided by the formation brine density to get the pore volume of each core. Porosity was then calculated using the pore and bulk volumes for each core. All these values are tabulated in Table 5.1.

Table 5.1: Properties of the cores used in the experiments

Experiment	Experiment 1	Experiment 2	Experiment 3	Experiment 4	Experiment 5	Experiment 6
Core Dia (cm)	3.81	3.78	3.77	3.77	3.77	3.81
Core Length (cm)	30.48	30.48	30.45	30.44	30.48	30.48
Core Bulk Volume (cm^3)	347.5	343	340	340	340.2	347.5
Core Dry Weight (g)	728	745	748	737	755.15	748
Core Wet Weight (g)	797	809	811.5	807.3	818.15	813
Core Pore Volume (cm^3)	60.82	55	55.15	61.7	55.12	56.5
Core Porosity (%)	17.5	16	16.2	18.16	16.2	16.26

5.1.2 CT Scan Measurements:

CT scan of the cores was performed for two of the experiments both before and after saturation with formation brine. The scan was also done for the brine sample to get the CT number of the brine. Porosity was calculated using the CT numbers obtained and the measurements were close to the porosity values obtained by weight method. The scan for experiment 6 was performed with a newer machine, which resulted in a much closer match of the porosity values. These values are tabulated in Table 5.2.

Table 5.2: CT scan results for Experiment 1 and 6

Experiment	**CT Number (dry core)**	**CT Number (saturated core)**	**CT Number (brine)**	**CT Number (air)**	**Porosity through CT scan (%)**	**Porosity through weight method (%)**
Experiment 1	2422.03	2227.67	356.29	-1000 (default)	14.3	16
Experiment 6	2534.06	2312.45	356.29	-1000 (default)	16.34	16.26

5.1.3 Oil Saturation

After each core was loaded in the system and re-saturated with formation brine at the desired pressure, the first flooding was performed with oil to displace the formation water, saturate the core with oil and establish Sw_i.

Oil was injected by means of an outside transfer cell that was connected to an ISCO pump which was used to inject the oil at the set flow rate of 0.25 cc/min. The produced fluids from the core were collected in graduated cylinders placed outside the oven through the core outlet line. Water recovery from the core was calculated after subtracting the dead

volume from the produced volume. The dead volume consisted of the outlet and the inlet tubing lines where the oil displaced the formation brine.

Initially when oil was injected there was almost a linear relationship between the injected oil and the produced water. However, once the oil breakthrough occurred, the water production declined drastically and eventually only oil was produced from the core. The oil injection was stopped at that point, however in each case, more than 1 PV of oil was injected. The oil breakthrough occurred between 0.6 PV to 0.8 PV injected. The initial water saturations for each of the core-flooding experiments are tabulated in Table 5.3 and the water recovery trends are shown in Figures 5.1, 5.2, 5.3, 5.4, 5.5 and 5.6.

Table 5.3: Initial Water Saturations for all the core-flooding experiments

Experiment	Experiment 1	Experiment 2	Experiment 3	Experiment 4	Experiment 5	Experiment 6
Initial Water Saturation (S_{wi})	41 %	30 %	21 %	25 %	24 %	34 %

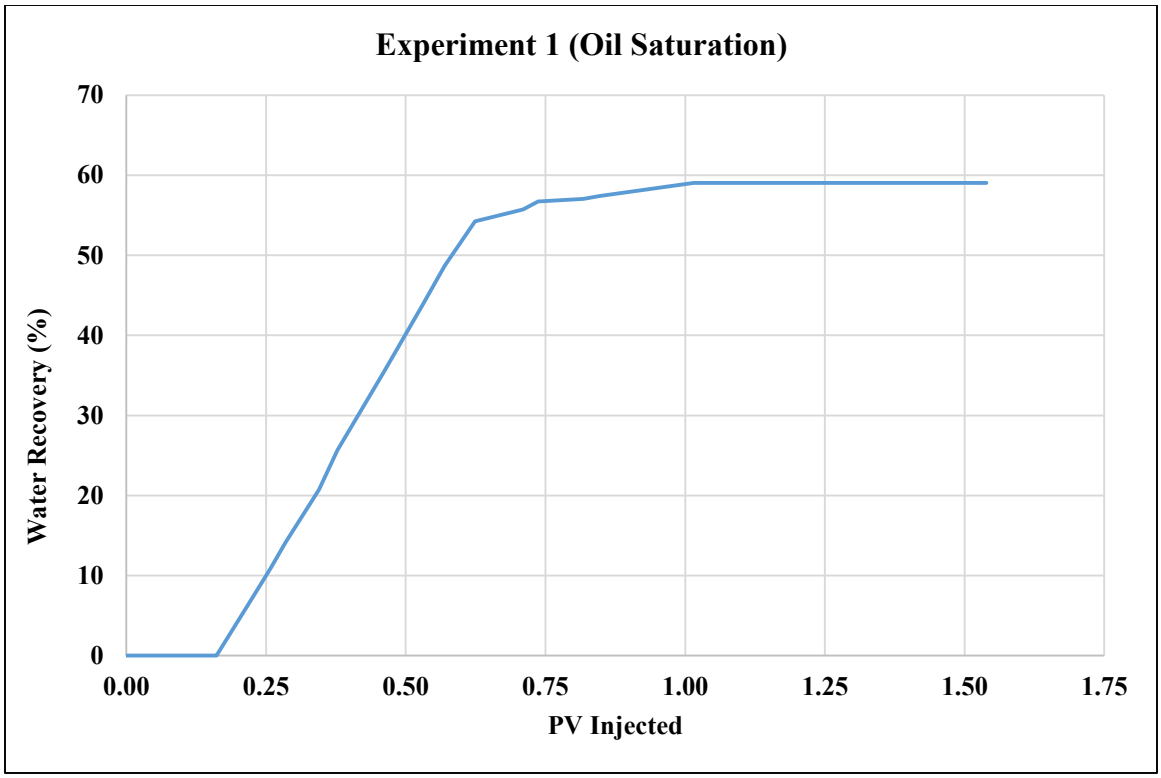


Figure 5.1: Oil saturation (Experiment 1)

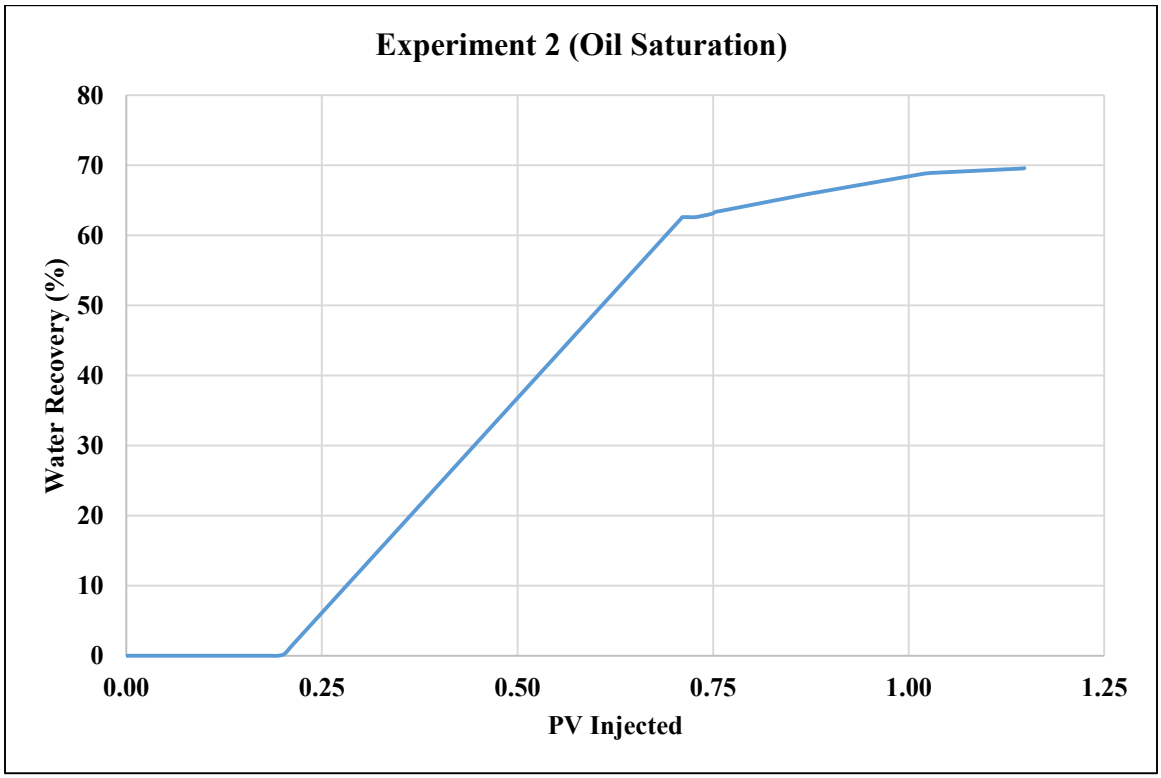


Figure 5.2: Oil saturation (Experiment 2)

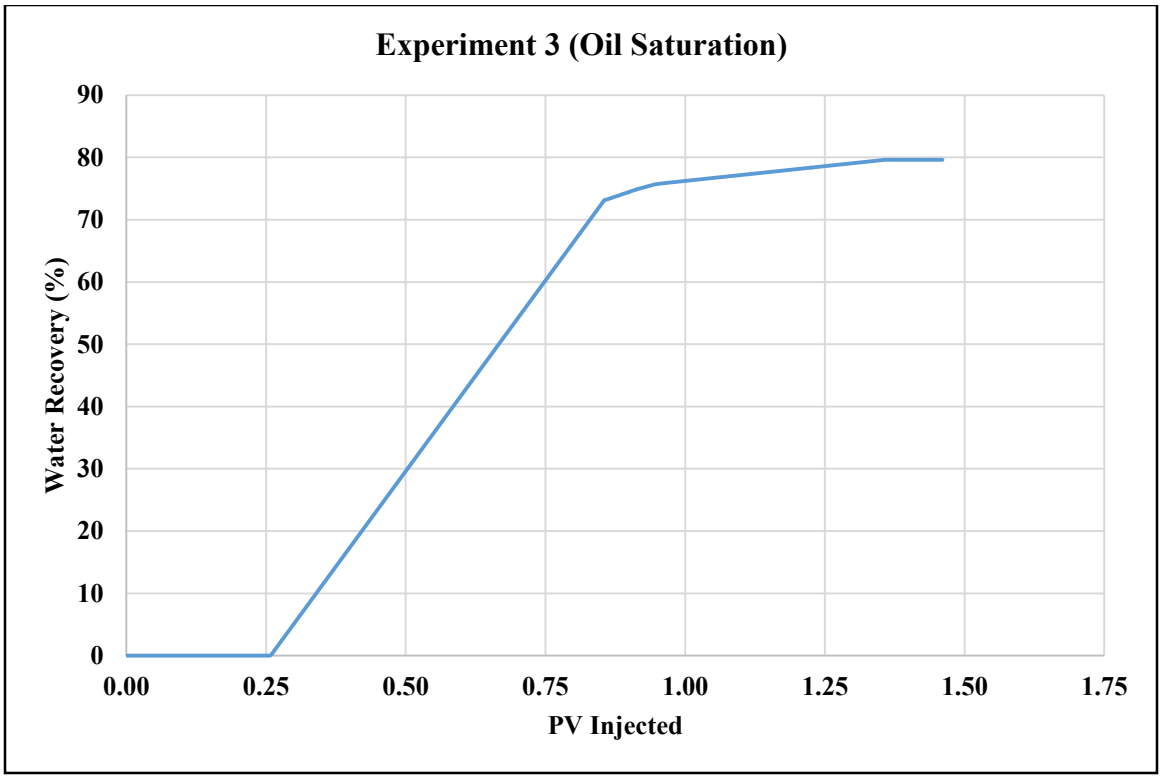


Figure 5.3: Oil saturation (Experiment 3)

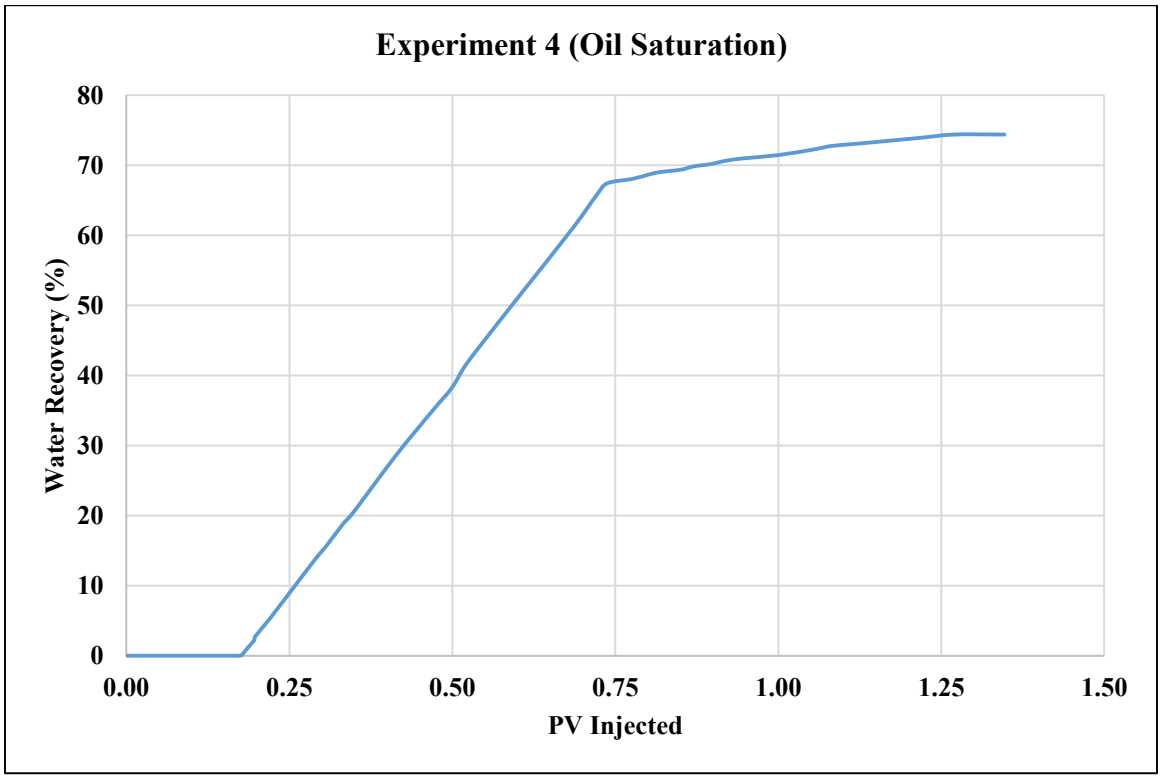


Figure 5.4: Oil saturation (Experiment 4)

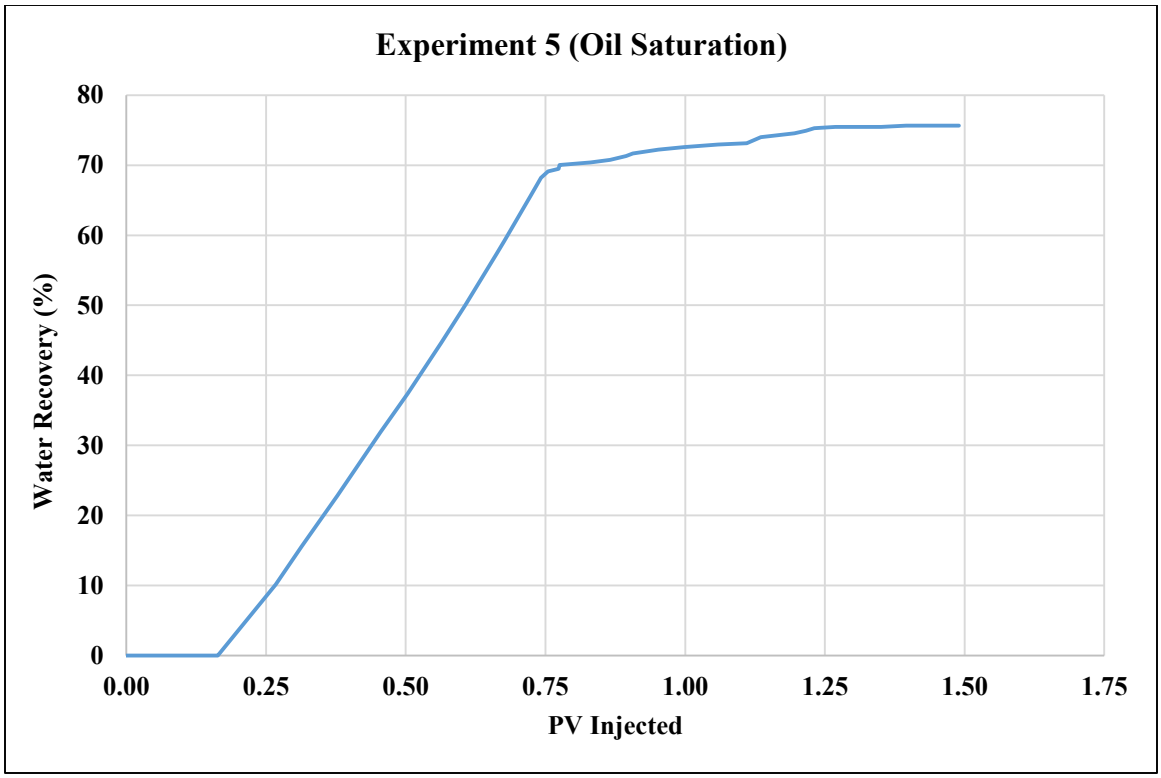


Figure 5.5: Oil saturation (Experiment 5)

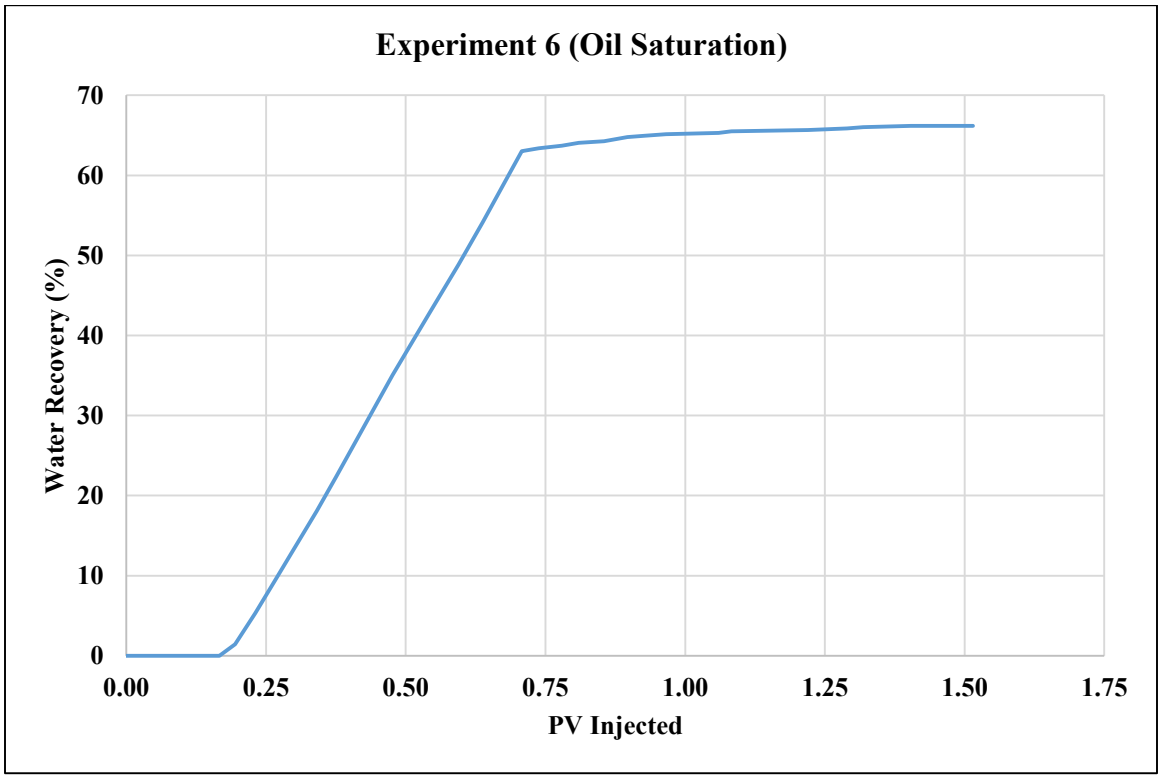


Figure 5.6: Oil saturation (Experiment 6)

5.1.4 Core-flooding experiments

After the aging period of 5 days, coreflooding was performed. The injection cycles were followed as described earlier. Based on the type of injection strategy, our corefloods can be classified into 3 different strategies. The base experiment of only CO_2 injection, alternate surfactant and CO_2 cycles and co-injection of surfactant and CO_2. In all the experiments, initially waterflooding was performed and another brine slug was injected at the end of the experiment. The total oil recovered from the core was calculated by subtracting the dead volume from the produced oil.

Figure 5.7: Example of samples collected during core-flooding experiment

The results of each of the experiments are detailed below.

5.1.4.1 Base Case- CO_2 Flooding

In this experiment the flooding was performed in the following manner:

1. 2 PV of brine (sea water).
2. 2.5 PV of CO_2.
3. 1 PV of brine (sea water).

The amount of oil recovered in each cycle is tabulated in Table 5.4.

Table 5.4: Oil Recovery (Experiment 1)

Cycle	**Pore Volume**	**Oil Recovery (%)**
1st Brine Flooding	2 PV	32
CO_2 Flooding	2.5 PV	26.2
2nd Brine Flooding	1 PV	2.5
Total	**5.5 PV**	**60.7**

The oil recovery and the delta P trend during the entire flooding are plotted in Figures 5.8 and 5.9.

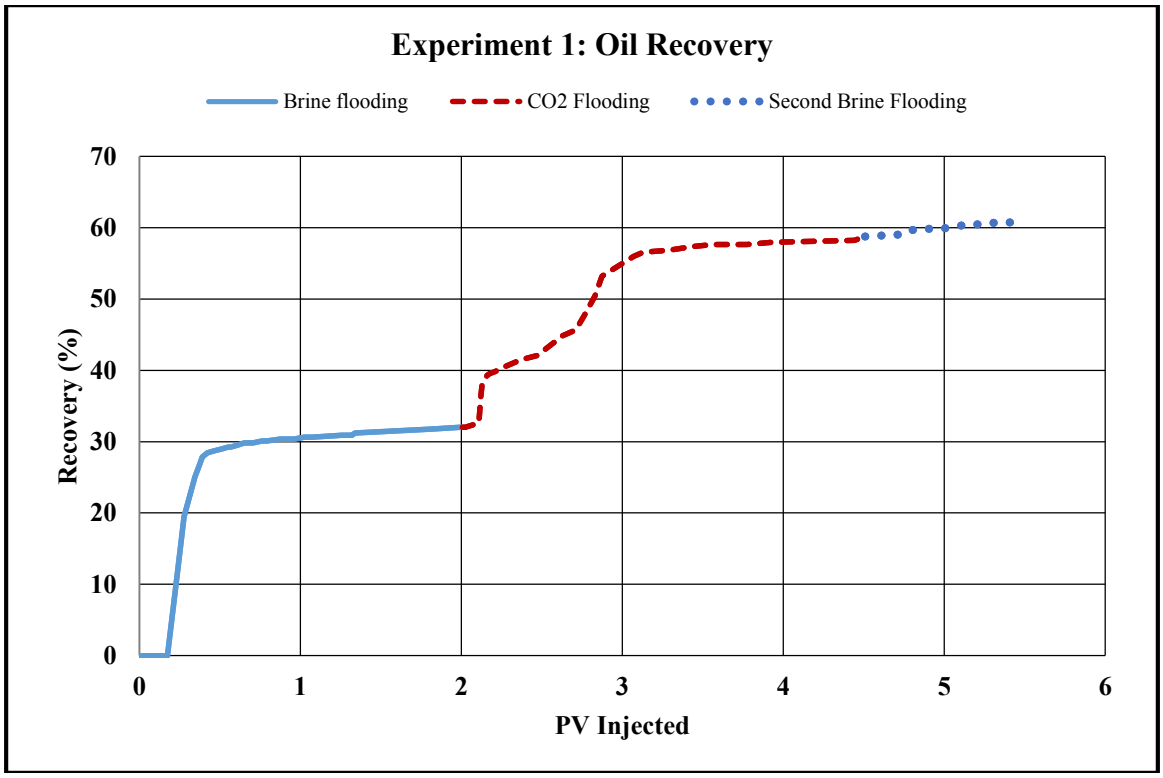


Figure 5.8: Oil recovery trend (Experiment 1)

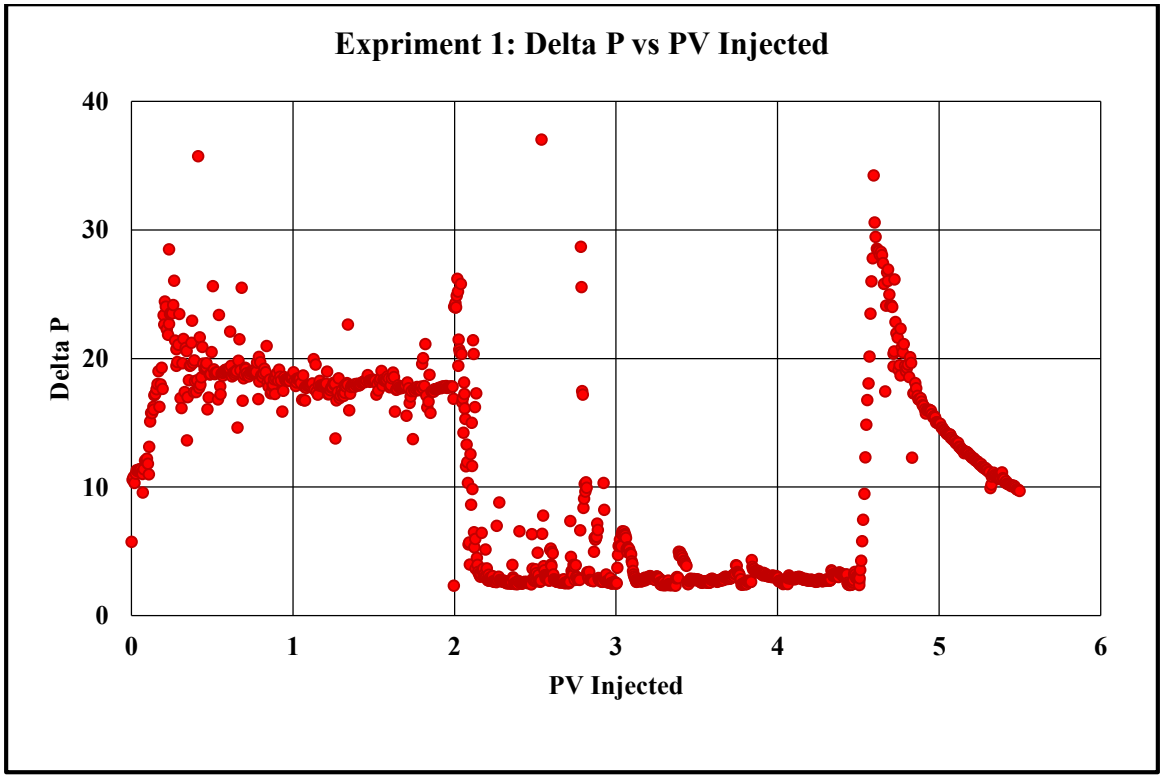


Figure 5.9: Pressure drop trend (Experiment 1)

5.1.4.2 Alternate Surfactant Solution and CO_2 Flooding

This type of experiments were conducted to study the effect of cycle size on the increment in oil recovery. Three experiments were performed using this strategy. The slug sizes were different in each experiment. The results of these experiments is given below.

5.1.4.2.1 Equal Slug Sizes

In this experiment the flooding was performed in the following manner:

1. 2 PV of brine (sea water).
2. 0.5 PV of surfactant solution.
3. 0.5 PV of CO_2.
4. 0.5 PV of surfactant solution.
5. 0.5 PV of CO_2.
6. 0.25 PV of surfactant solution.
7. 0.25 PV of CO_2.
8. 1 PV of brine (sea water).

The amount of oil recovered in each cycle is tabulated in Table 5.5.

Table 5.5: Oil Recovery (Experiment 2)

Cycle	**Pore Volume**	**Oil Recovery (%)**
1st Brine Flooding	2 PV	25.2
Surfactant Solution Flooding	0.5 PV	1
CO_2 Flooding	0.5 PV	7.2
Surfactant Solution Flooding	0.5 PV	8
CO_2 Flooding	0.5 PV	1
Surfactant Solution Flooding	0.25 PV	2.66
CO_2 Flooding	0.25 PV	1
2nd Brine Flooding	1 PV	5.3
Total	**5.5 PV**	**51.6**

The oil recovery and the delta P trend during the entire flooding are plotted in Figures 5.10 and 5.11.

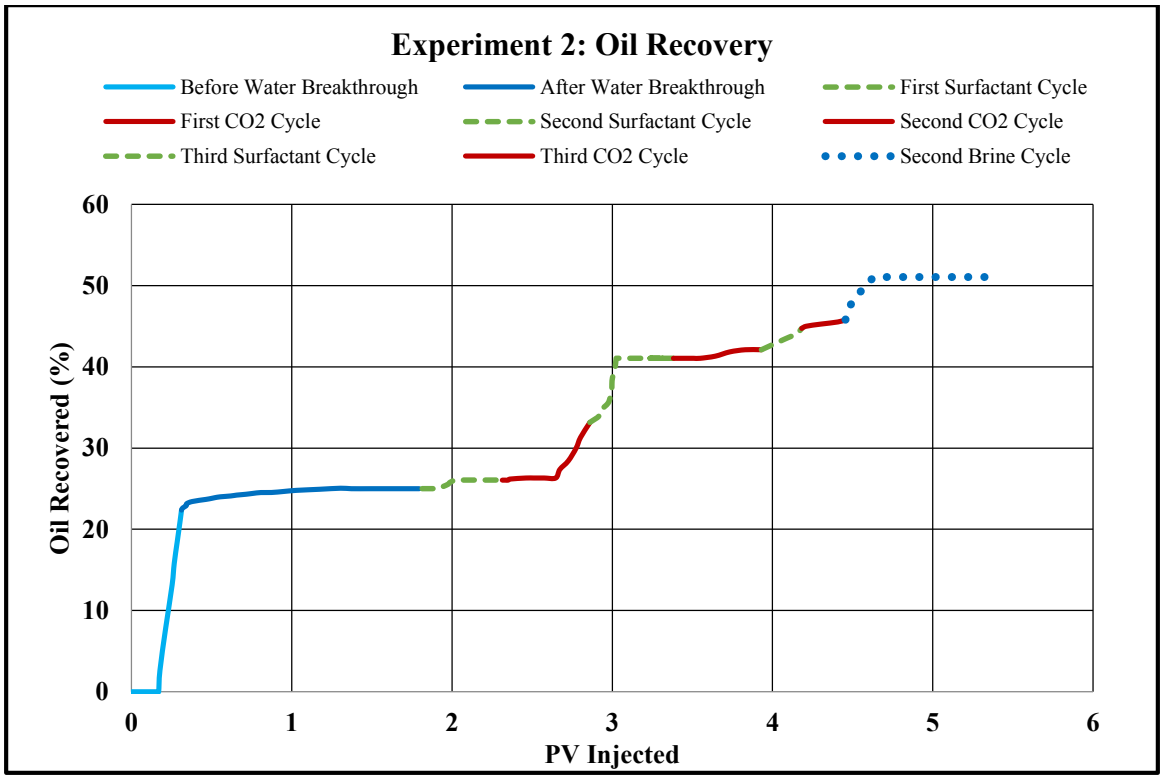


Figure 5.10: Oil recovery trend (Experiment 2)

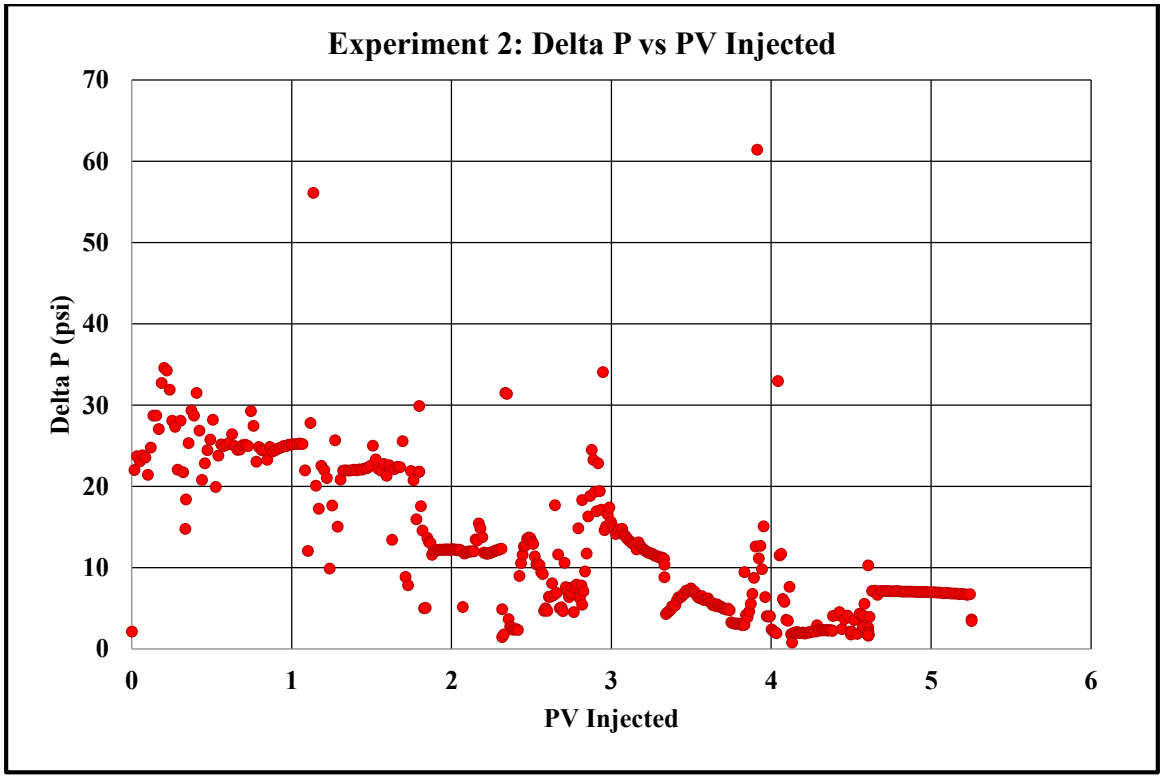


Figure 5.11: Pressure drop trend (Experiment 2)

5.1.4.2.2 Larger CO_2 Slug Sizes

In this experiment the flooding was performed in the following manner:

1. 2 PV of brine (sea water).
2. 0.25 PV of surfactant solution.
3. 0.75 PV of CO_2.
4. 0.25 PV of surfactant solution.
5. 0.75 PV of CO_2.
6. 0.125 PV of surfactant solution.
7. 0.375 PV of CO_2.
8. 1 PV of brine (sea water).

The amount of oil recovered in each cycle is tabulated in Table 5.6.

Table 5.6: Oil Recovery (Experiment 3)

Cycle	**Pore Volume**	**Oil Recovery (%)**
1st Brine Flooding	2 PV	33.2
Surfactant Solution Flooding	0.25 PV	2
CO_2 Flooding	0.75 PV	10.25
Surfactant Solution Flooding	0.25 PV	5.5
CO_2 Flooding	0.75 PV	2.3
Surfactant Solution Flooding	0.125 PV	2.3
CO_2 Flooding	0.375 PV	4.5
2nd Brine Flooding	1 PV	6.8
Total	**5.5 PV**	**67**

The oil recovery and the delta P trend during the entire flooding are plotted in Figures 5.12 and 5.13.

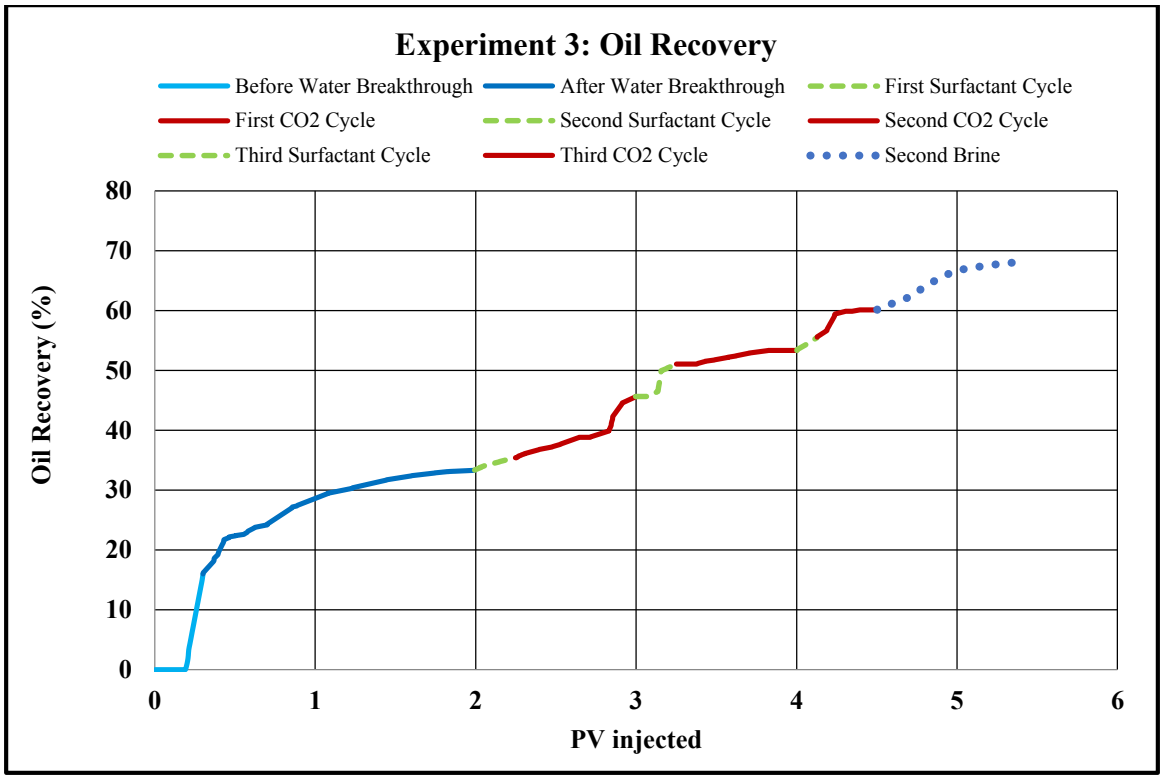


Figure 5.12: Oil recovery trend (Experiment 3)

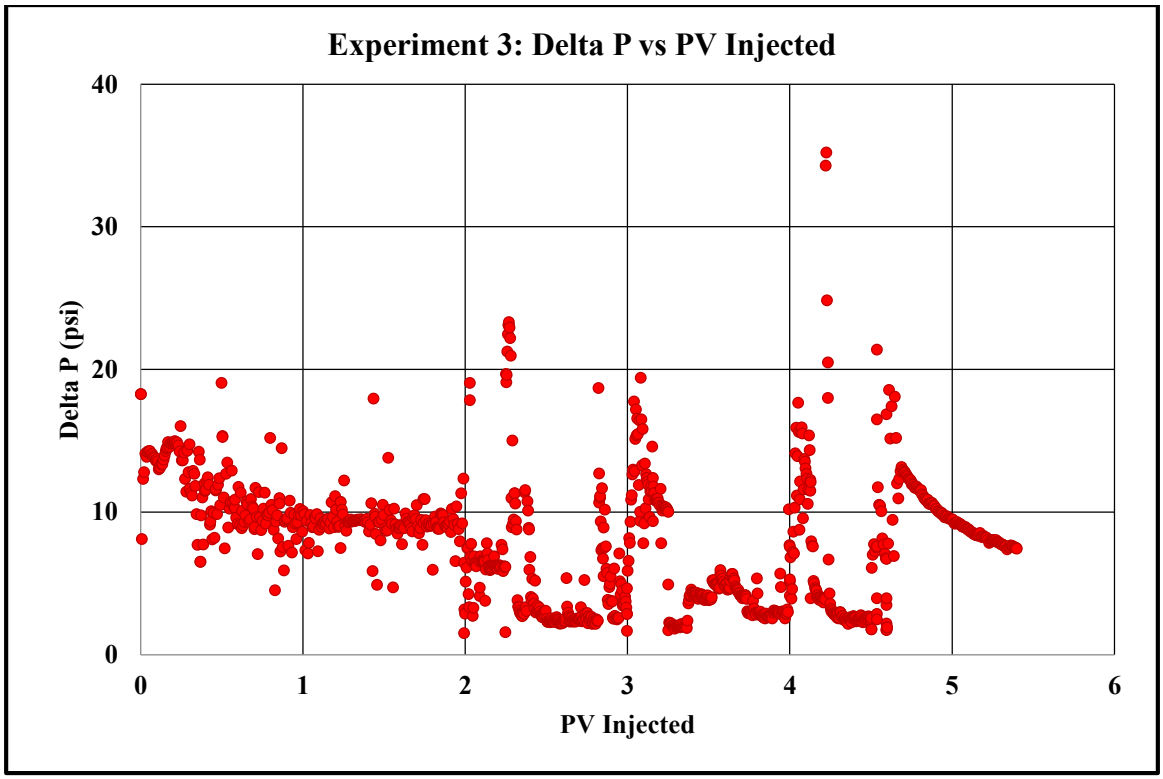


Figure 5.13: Pressure drop trend (Experiment 3)

5.1.4.2.3 Larger Surfactant Solution Slug Sizes

In this experiment the flooding was performed in the following manner:

1. 2 PV of brine (sea water).
2. 0.75 PV of surfactant solution.
3. 0.25 PV of CO_2.
4. 0.75 PV of surfactant solution.
5. 0.25 PV of CO_2.
6. 0.375 PV of surfactant solution.
7. 0.125 PV of CO_2.
8. 1 PV of brine (sea water).

The amount of oil recovered in each cycle is tabulated in Table 5.7.

Table 5.7: Oil Recovery (Experiment 4)

Cycle	**Pore Volume**	**Oil Recovery (%)**
1st Brine Flooding	2 PV	41.18
Surfactant Solution Flooding	0.75 PV	1.3
CO_2 Flooding	0.25 PV	23.75
Surfactant Solution Flooding	0.75 PV	3.5
CO_2 Flooding	0.25 PV	0
Surfactant Solution Flooding	0.375 PV	0
CO_2 Flooding	0.125 PV	0
2nd Brine Flooding	1 PV	0
Total	**5.5 PV**	**69.7**

The oil recovery and the delta P trend during the entire flooding are plotted in Figures 5.14 and 5.15.

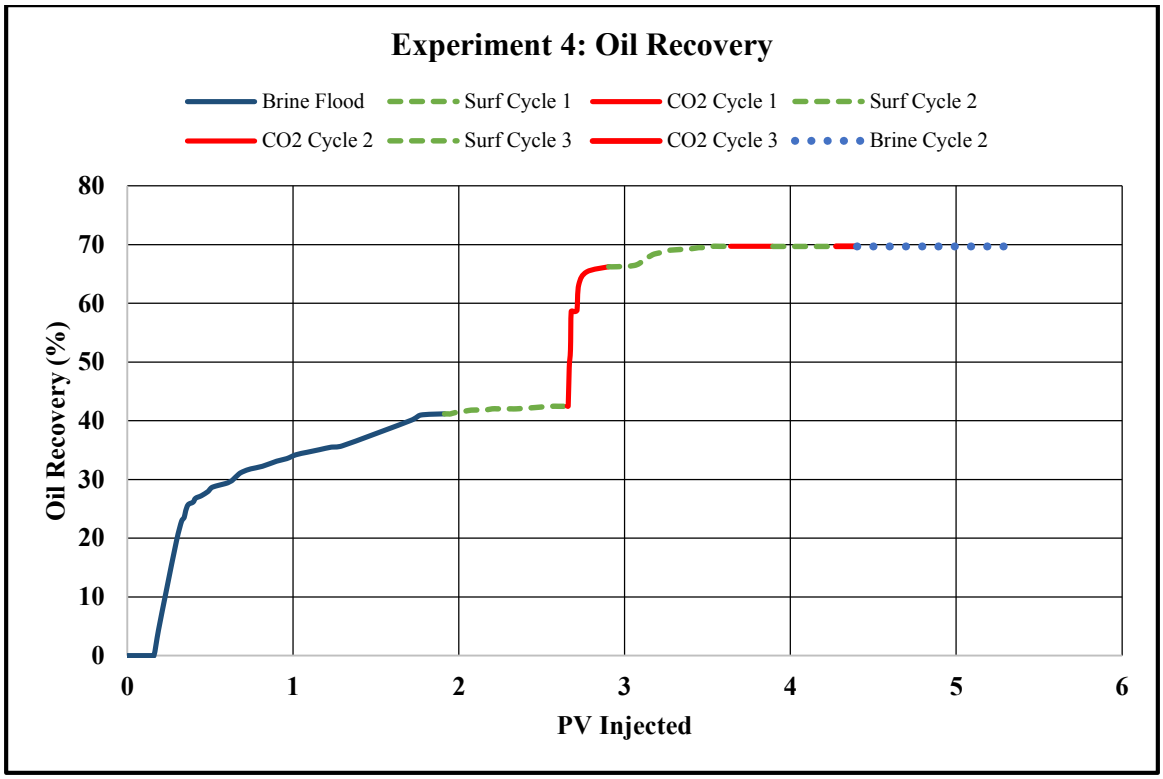


Figure 5.14: Oil recovery trend (Experiment 4)

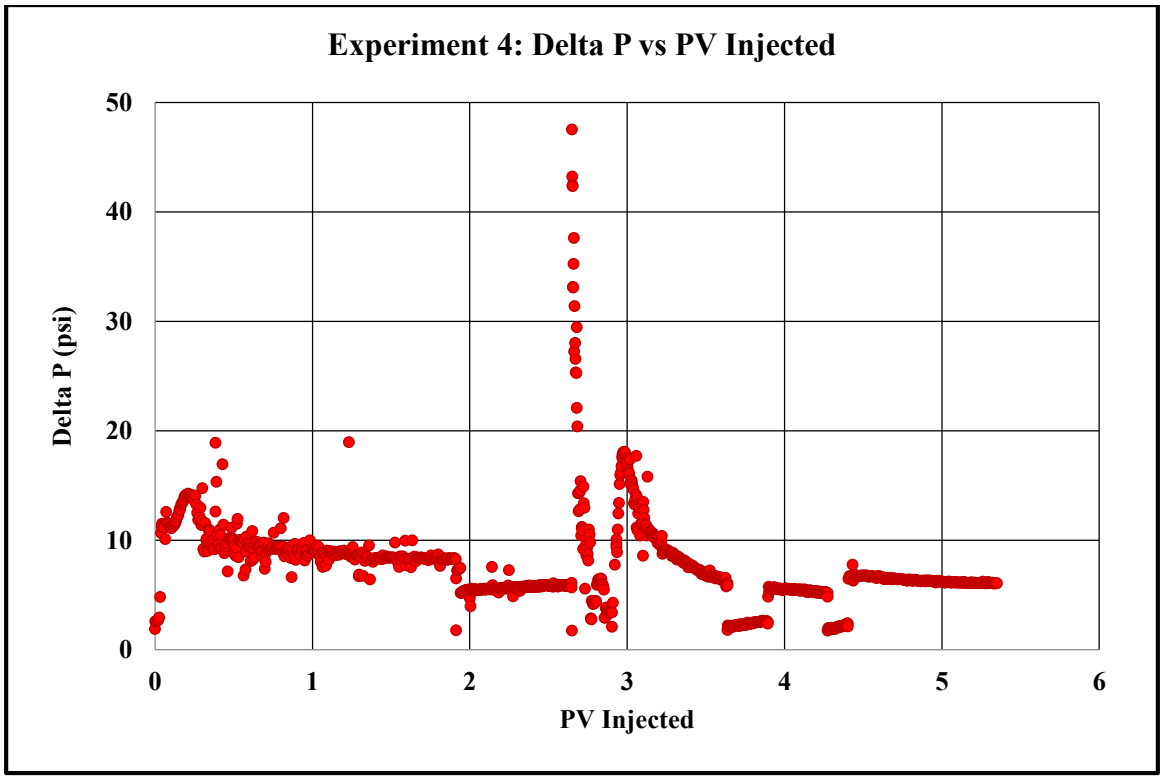


Figure 5.15: Pressure drop trend (Experiment 4)

5.1.4.3 Combined Surfactant Solution and CO_2 Flooding

This type of experiments were conducted to study the effect of co-injection of the two fluids and possible formation of foam on the increment in oil recovery. Two experiments were performed using this strategy. The surfactants were different in each experiment. The results of these experiments is given below.

5.1.4.3.1 Co-injection using fluoro-surfactant

In this experiment the flooding was performed in the following manner:

1. 2 PV of brine (sea water).
2. 2.5 PV of Surfactant Solution and CO_2.
3. 1 PV of brine (sea water).

The amount of oil recovered in each cycle is tabulated in Table 5.8.

Table 5.8: Oil Recovery (Experiment 5)

Cycle	Pore Volume	Oil Recovery (%)
1st Brine Flooding	2 PV	39.5
Surfactant-CO_2 Flooding	2.5 PV	24.3
2nd Brine Flooding	1 PV	2.6
Total	**5.5 PV**	**66.4**

The oil recovery and the delta P trend during the entire flooding are plotted in Figures 5.16 and 5.17.

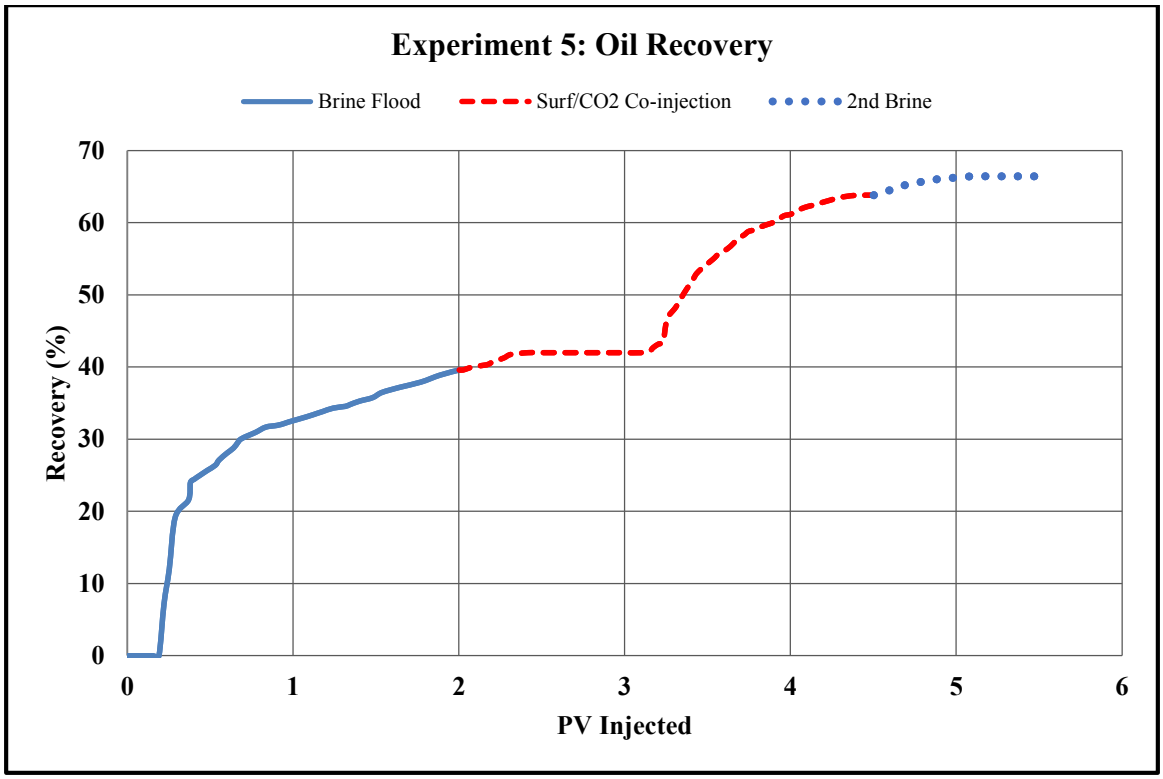


Figure 5.16: Oil recovery trend (Experiment 5)

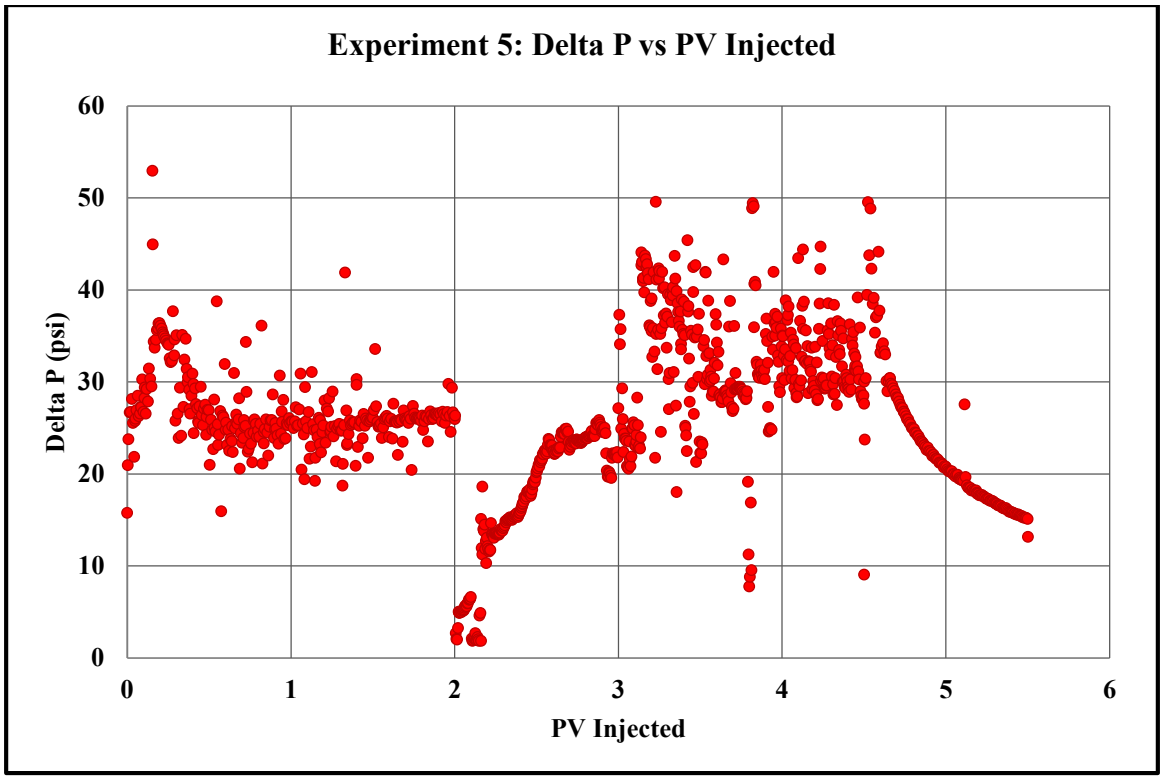


Figure 5.17: Pressure drop trend (Experiment 5)

5.1.4.3.2 Co-injection using Ethomeen

In this experiment the flooding was performed in the following manner:

1. 2 PV of brine (sea water).
2. 2.5 PV of Surfactant Solution and CO_2.
3. 0.15 PV of brine (sea water).

The second brine cycle could not be completed due to a problem in the BPR. Since this experiment was conducted to compare the performance with the fluoro-surfactant, thus the comparison for the two experiments was done on the basis of the surfactant-CO_2 co-injection cycle. The amount of oil recovered in each cycle is tabulated in Table 5.9.

Table 5.9: Oil Recovery (Experiment 6)

Cycle	**Pore Volume**	**Oil Recovery (%)**
1st Brine Flooding	2 PV	37
Surfactant-CO_2 Flooding	2.5 PV	18
2nd Brine Flooding	1 PV	3
Total	**5.5 PV**	**58**

The oil recovery and the delta P trend during the entire flooding are plotted in Figures 5.18 and 5.19.

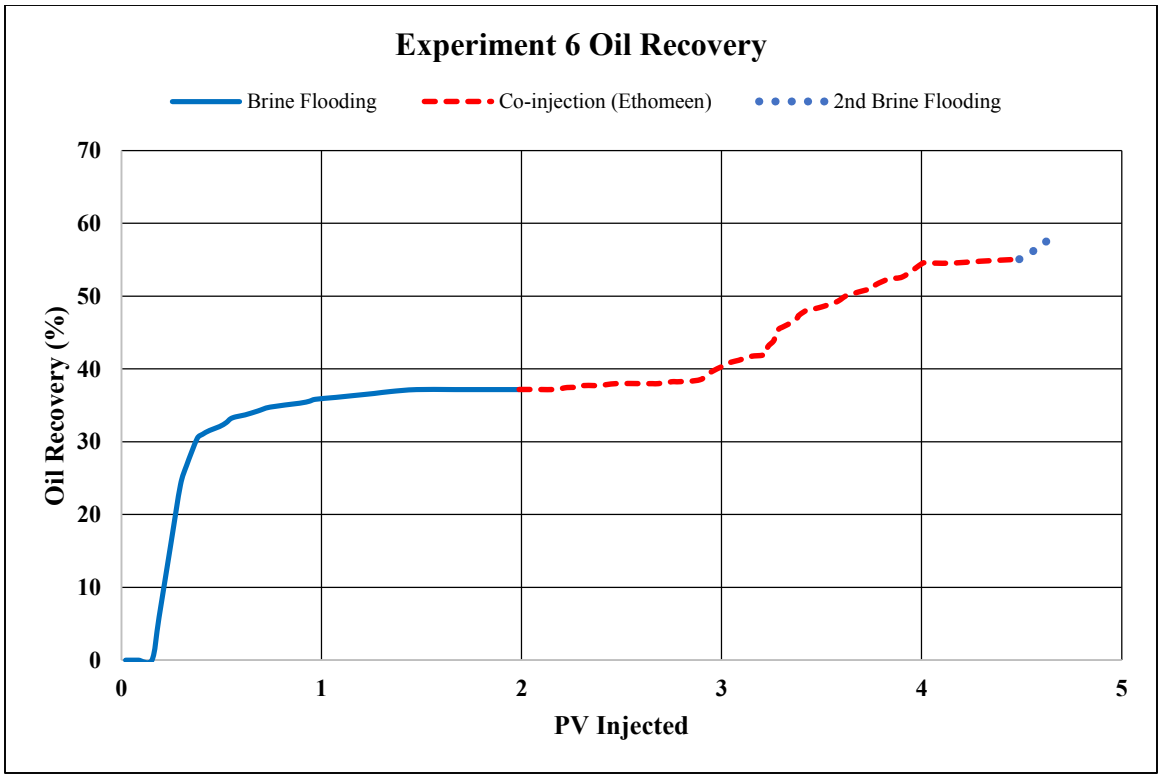


Figure 5.18: Oil Recovery trend (Experiment 6)

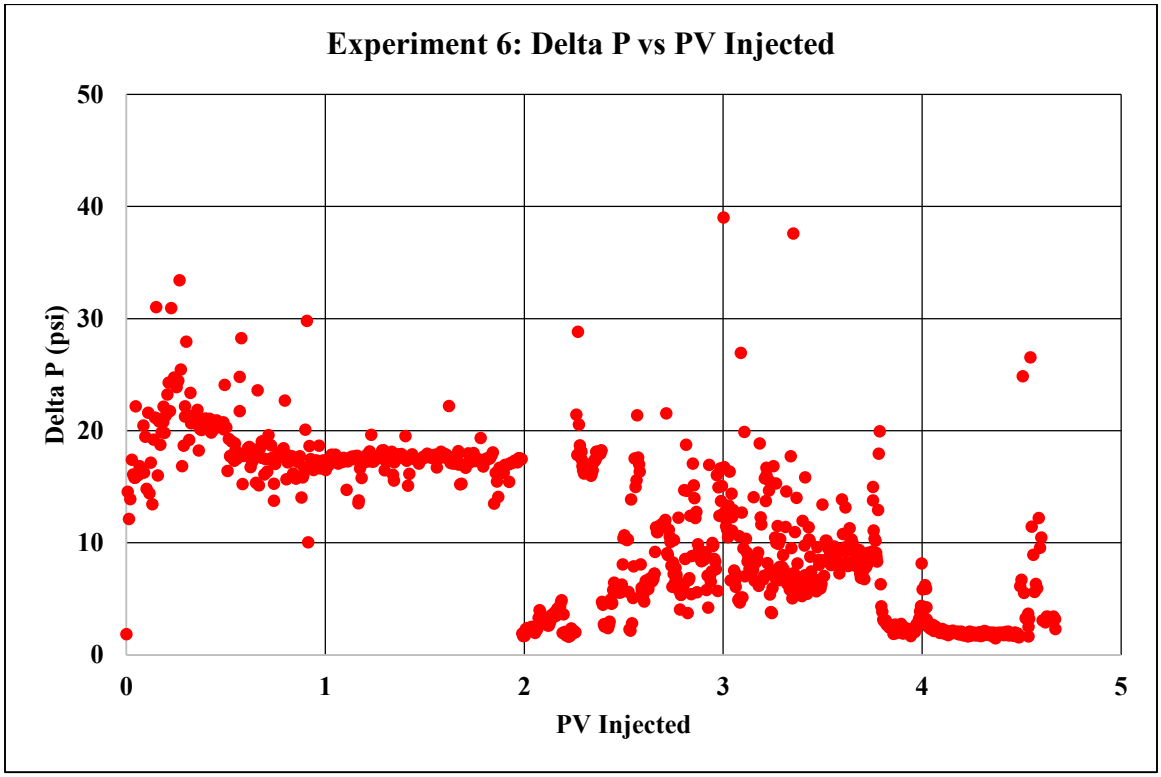


Figure 5.19: Pressure drop trend (Experiment 6)

5.1.4.4 Summary of Core-flooding Results

The results of all the coreflooding experiments are summarized in Table 5.10. The RF efficiency is the amount of oil recovered from the oil left in the core after the first brine flood.

Table 5.10: Summary of Core-flooding results

Experiment	Experiment 1	Experiment 2	Experiment 3	Experiment 4	Experiment 5	Experiment 6
Total Oil Recovery	60.72 %	51.6 %	67 %	69.7 %	66.4 %	58 %
RF efficiency after brine flood	43.8 %	34.7 %	52 %	48 %	44.4 %	32.7 %

5.2 Discussion of Core-flooding Results

The base case of only using CO_2 after the first brine flood, gave a significant rise in the oil recovery. This indicates that CO_2 itself is quite effective in increasing oil recovery. However, the effectiveness of CO_2 could increase if its mobility is reduced enabling higher contact with the oil. To do so, in all the next experiments, a surfactant was used with the CO_2 in different combinations, to see if it provides any additional increment in oil recovery.

5.2.1 Effect of Slug Size on oil recovery

As described earlier, three experiments using the alternate surfactant solution and CO_2 injection strategy were performed. The total PV injected was same (2.5 PV), but the individual slug sizes were changed. In all the three experiments the maximum increment in the oil recovery was observed during the first and second cycle. The first injected CO_2

slug and the surfactant solution slug immediately after, produced the largest quantity of oil. The increment in oil recovery after the first brine flooding and the contribution of the first CO_2 and the surfactant solution slug immediately after, for each of the three experiments is tabulated in Table 5.11.

Table 5.11: Comparison of alternate core-flooding experiments

Experiment	**Experiment 2**	**Experiment 3**	**Experiment 4**
Increment in oil recovery after first brine flood (%)	26.4	33.8	27.9
Contribution of 1st CO_2 and 2nd surfactant solution slugs (%)	57.5	46.6	97.6

The biggest increment in the recovery factor after brine flooding (~34%) was observed in Experiment 3 where the CO_2 slug size was bigger than the surfactant slug size. The highest total recovery was obtained for Experiment 4 where a bigger surfactant solution slug size was injected prior to the CO_2 slug. This experiment also exhibited a different trend in which all the oil was recovered in the first three half-cycles with no oil recovery in the next cycles. This showed that the recovery can be obtained much quickly if this strategy is followed. On the contrary, in Experiment 3 where the CO_2 slug size is bigger, oil continues to come till the last cycle. This experiment gave the highest increment in oil recovery after brine flooding (~34%) and supports the argument that CO_2 plays a bigger role in mobilizing and producing the oil than the surfactant solution. Experiment 2, was performed keeping the slug sizes equal. This experiment gave the lowest total oil recovery among all the experiments. However this low recovery was due to the low recovery obtained during the first brine cycle. The increment in the oil recovery during the surfactant solution-CO_2

cycles was similar to the other experiments. This experiment showed that even if the oil recovery is low after secondary recovery process, the surfactant-CO_2 system is effective in increasing the oil recovery. The second brine flood which was conducted at the end of the experiments also contributed to the increase in oil recovery in Experiments 2 and 3. This increase was as a result of the brine displacing the oil in the tubing lines from the core outlet to the fluid collection point which had been recovered during the CO_2 slug prior to the brine flood. Figure 5.20 shows the comparison of the three alternating strategy experiments.

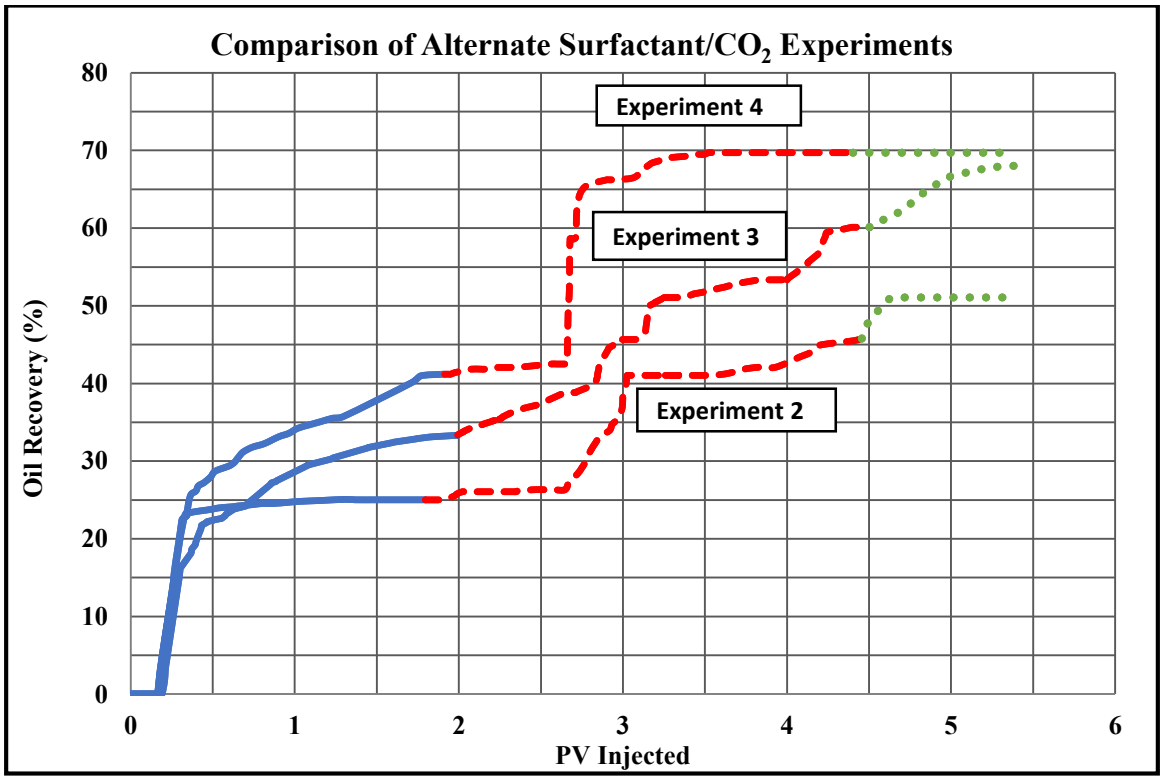


Figure 5.20: Comparison of oil recovery for the alternating strategy experiments

5.2.2 Effect of co-injection

The next injection strategy followed was the simultaneous injection of surfactant solution and CO_2. Both the fluids were injected at the same flow rate together into the core. Using

this scheme, two experiments were conducted. In the first experiment, the same fluoro-surfactant was used that was used in the alternating cycle experiments, while in the second experiment a different surfactant was used. This enabled us to compare the injection schemes, as well as the two surfactants. The oil recovery trend for both the experiments was similar using this strategy. At the start of the flooding cycle, there was very little oil recovery. The recovery started to increase after around 1 PV of fluid had been injected and oil continued to produce till around 2 PV on the fluids was injected. The fluoro-surfactant CO_2 combination had a higher recovery than the ethomeen-CO_2 combination. Table 5.12 and Figure 5.21 show the comparison between the two experiments.

Table 5.12: Comparison of co-injection experiments

Experiment	**Experiment 5**	**Experiment 6**
Total Oil Recovery (%)	66.4	58
Oil Recovery during surf-CO_2 flooding	24.3	18

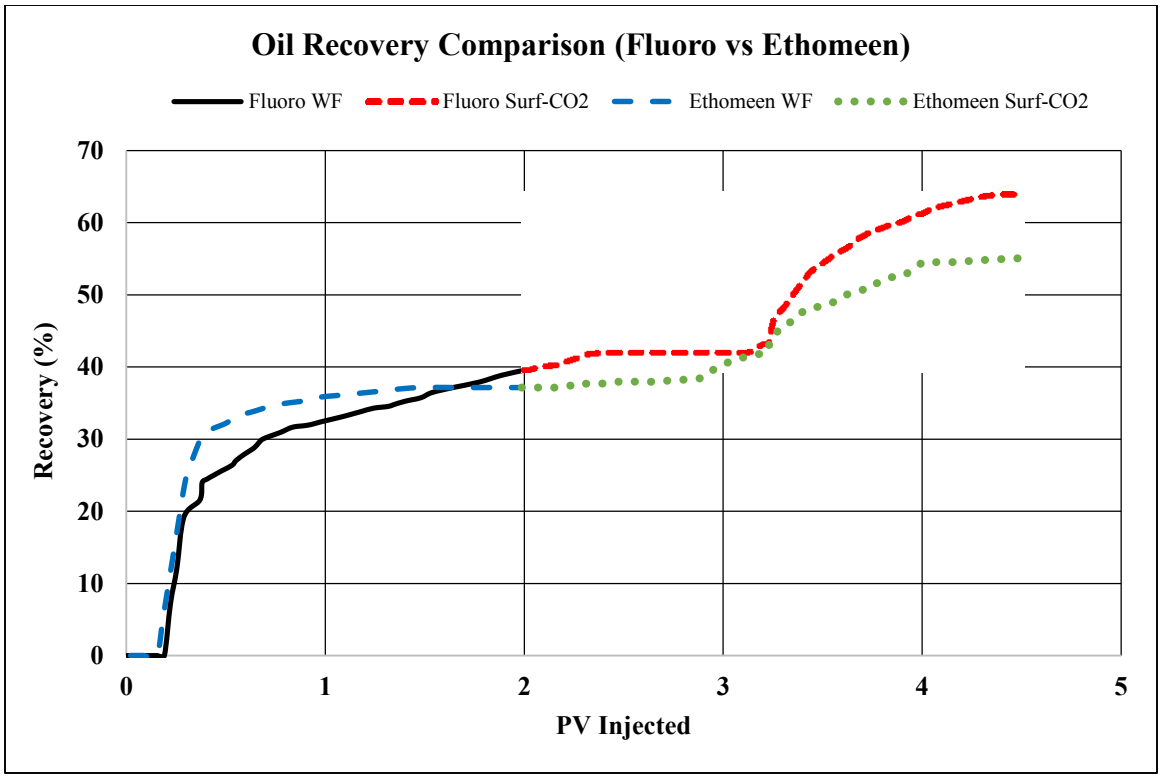


Figure 5.21: Oil recovery comparison of the co-injection experiments

The co-injection experiment did not gave a significant difference in total oil recovery compared to the alternating experiments. However the breakthrough of CO_2 was delayed in this strategy, which could be a positive factor if this strategy is applied on the field scale.

5.2.3 Pressure Drop Response and Foam Generation Concept

As with the case with earlier works done [29] [39], in all the alternate flooding experiments there was no indication of foam generation by the pressure drop response shown in Figures 5.11, 5.13 and 5.15. This can be due to the high saline environment [49], high temperature [50], presence of oil [51] [52] or the low concentration of surfactant in the solution [12]. All these factors hinder the generation and propagation of foam through surfactants and CO_2 in porous media. An increase in pressure drop was nevertheless evident when we had

high oil recovery. Some researchers have associated this short time of higher delta P to be a sign of foam generation. However recent researches suggest that stable foam should give a continuous high delta P, which was observed in the continuous fluorosurfactant-CO_2 flooding experiment. After injection of around 1.2 PV of continuous surfactant-CO_2 slug, the pressure drop increased and remained high during the rest of the flooding cycle. This high delta P matched the increment in oil recovery perfectly as shown in Figures 5.16 and 5.17. This experiment showed that foam can be generated by the surfactant solution and CO_2 even in typical reservoir conditions, provided a sufficient volume of the slug is injected. This behavior is in concurrence with recent studies [46] [39]. The total recovery factor for this experiment was similar to the alternate flooding experiments, which shows that foam is not always necessary for the increment in oil recovery. Rather it is the combination of the sc-CO_2 and the fluoro-surfactant system that makes the oil movable and producible. The pressure drop during the co-injection experiment using ethomeen surfactant was not as high as the pressure drop during the fluorosurfactant co-injection experiment. This indicates that there was no sign of a stable foam using this surfactant and that the surfactant was unstable at high temperature and high salinity. This also caused the recovery of oil to be lower for this experiment. The pressure drop response comparison for the two co-injection experiments is shown in Figure 5.22.

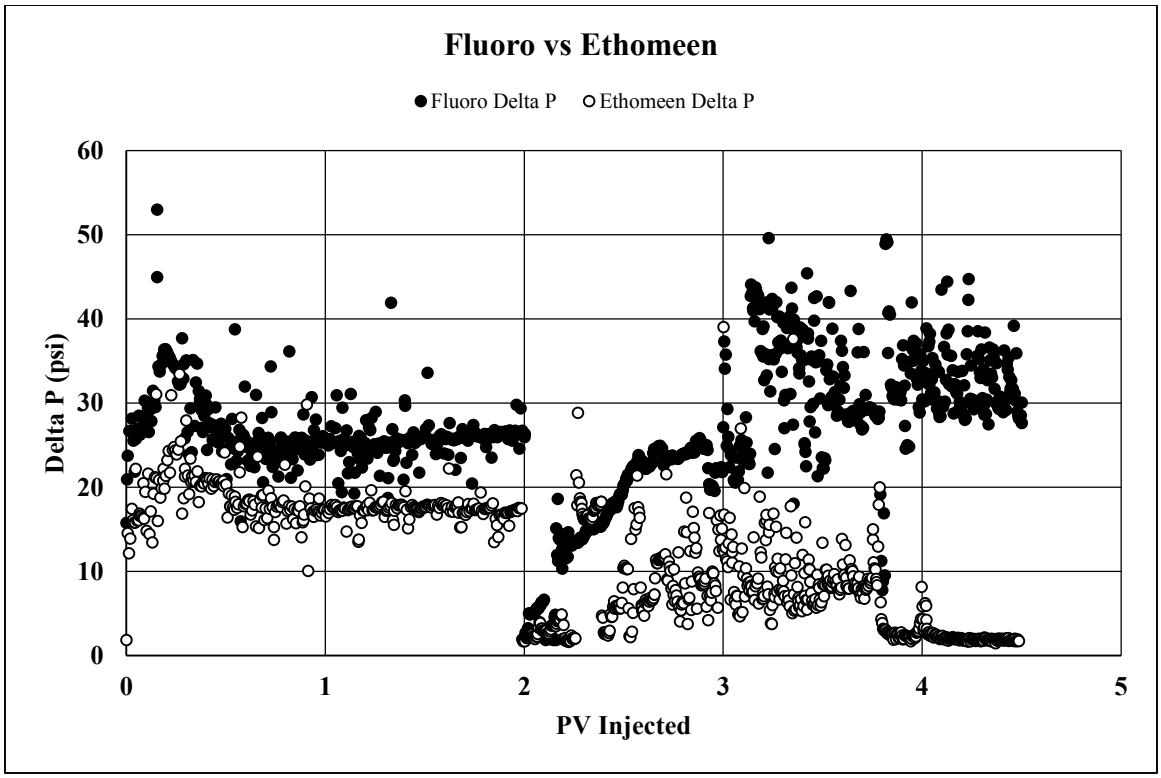


Figure 5.22: Pressure drop comparison of the co-injection experiments

5.3 IFT Results

5.3.1 Density Measurements

To calculate the Interfacial tension between any two fluids, the density of both the fluids had to be measured at the particular condition. The density of the injection brine (sea water), the surfactant solution and the oil were measured at 90°C and five different pressures. The density meter was first calibrated at all these conditions using two fluids of known densities, i.e. nitrogen and distilled water. The values of the densities of all the fluids is tabulated in Table 5.13.

Table 5.13: Density values of the reference and measured fluids

	Density at 90°C (g/ml)				
	Reference Fluids		Measured Fluids		
Pressure (psi)	**Distilled Water**	**Nitrogen**	**Sea Water**	**Sea Water + Fluoro**	**Oil**
500	0.96684	0.031782	1.00813	1.00708	0.84106
1000	0.968394	0.062914	1.00999	1.00976	0.84368
1800	0.970852	0.110381	**1.01176**	**1.01124**	**0.84632**
2500	0.972975	0.149604	1.01431	1.01385	0.85022
4000	0.977441	0.224531	1.01943	1.01822	0.85584

The density of all the fluids increased slightly with the pressure. The trend for each of the measured fluids is shown in Figures 5.23, 5.24 and 5.25.

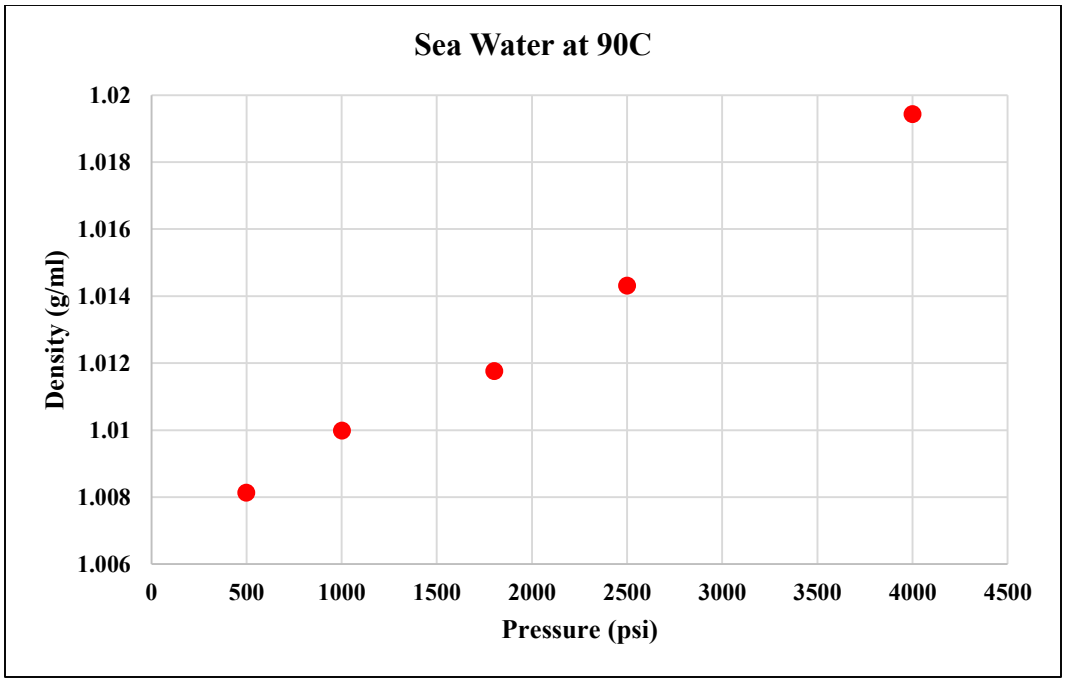


Figure 5.23: Density of sea water (injection brine) at 90°C

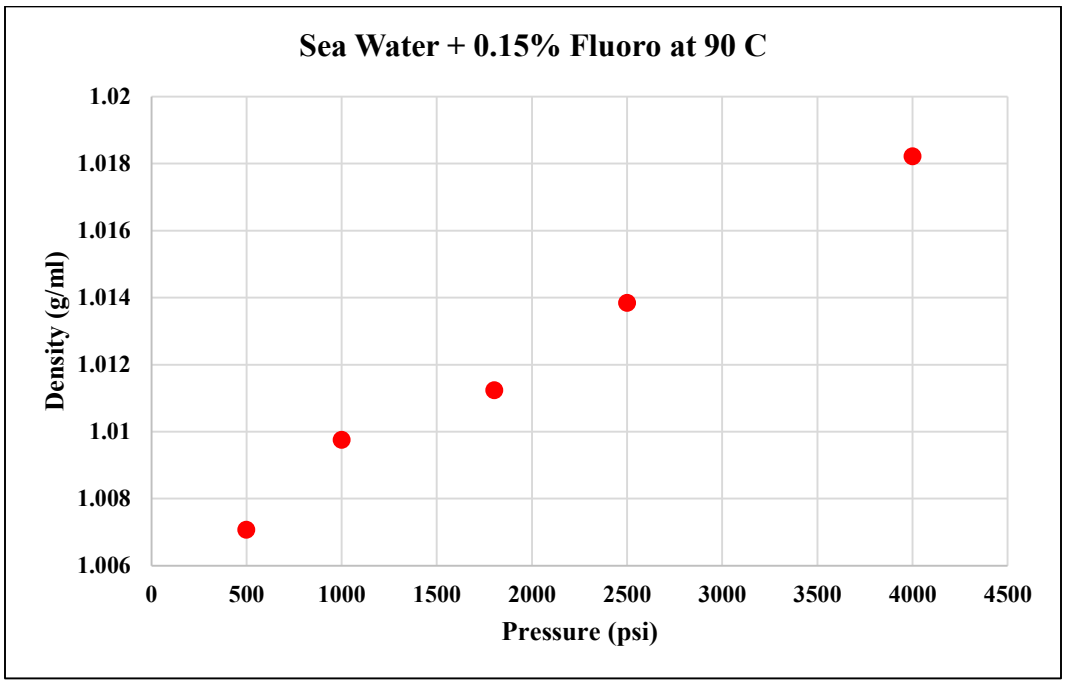


Figure 5.24: Density of surfactant solution at 90°C

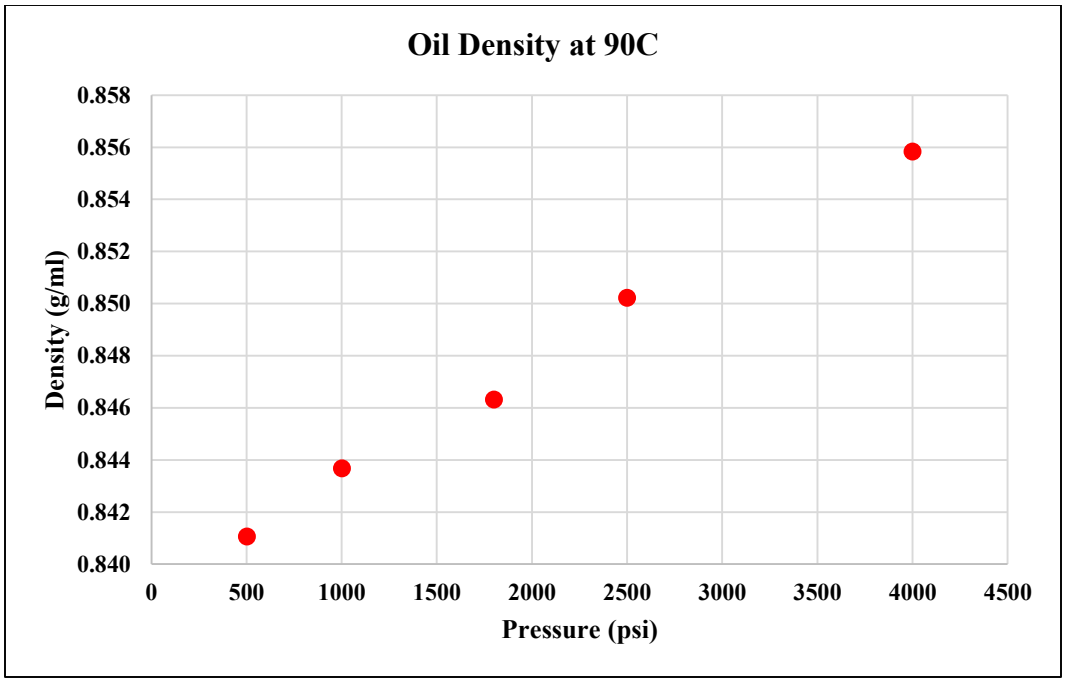


Figure 5.25: Density of dead oil at 90°C

5.3.2 IFT Measurements:

IFT measurements were done firstly between the injected brine (sea-water) and the dead oil used in the core-flooding and secondly between the surfactant solution and the dead oil. Oil drop was created in the bulk fluids that were the injection brine and the surfactant solution respectively. After each drop was created, a transition period was seen in which the IFT dropped rapidly and then stabilized at a "quasi-static value". This initial time dependence of the IFT value has been observed in a number of earlier studies and is attributed to equilibration between the two fluids [53].

Each drop was monitored for at least 600 seconds and the IFT value was measured by averaging the IFT values during the last 300 seconds for each drop. The results and images of the drops were saved every five seconds by the software on the computer attached to the

IFT equipment. The images, values and trends of the IFT measurements are shown in Table 5.14 and the Figures below.

Table 5.14: IFT measurements

IFT (mN/m)		
Pressure	**SW + Oil**	**0.15 % Fluoro in SW + oil**
500	19.22	4.49
1000	19.01	4.68
1800	**18.54**	**4.96**
2500	17.8	5.36
4000	17.7	5.56

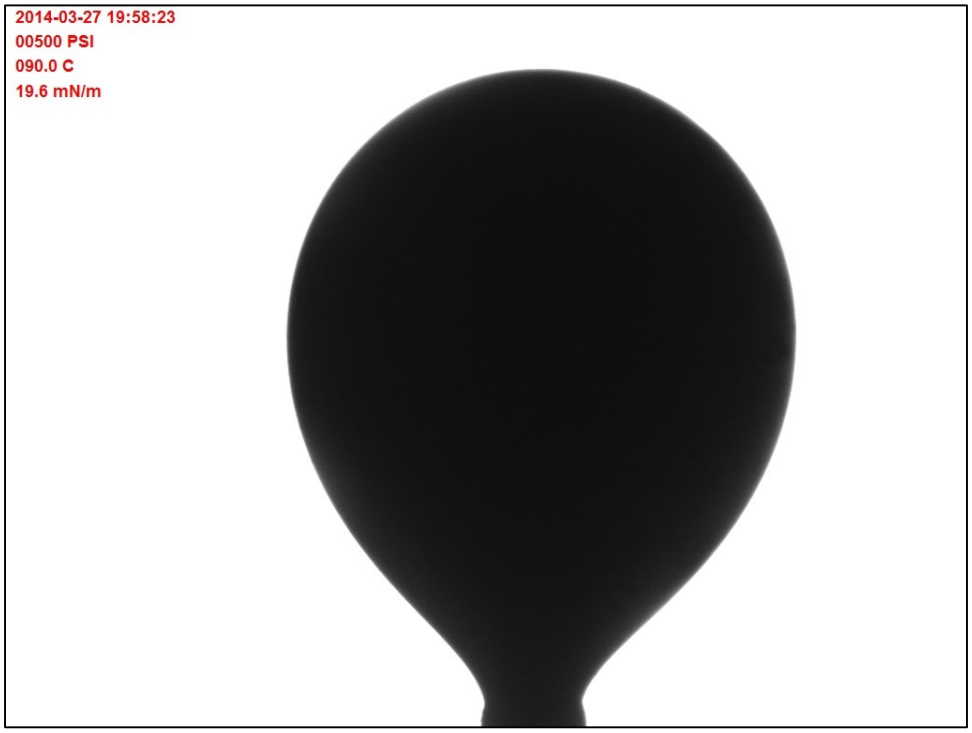


Figure 5.26: Shape of oil drop in sea water at 500 psi

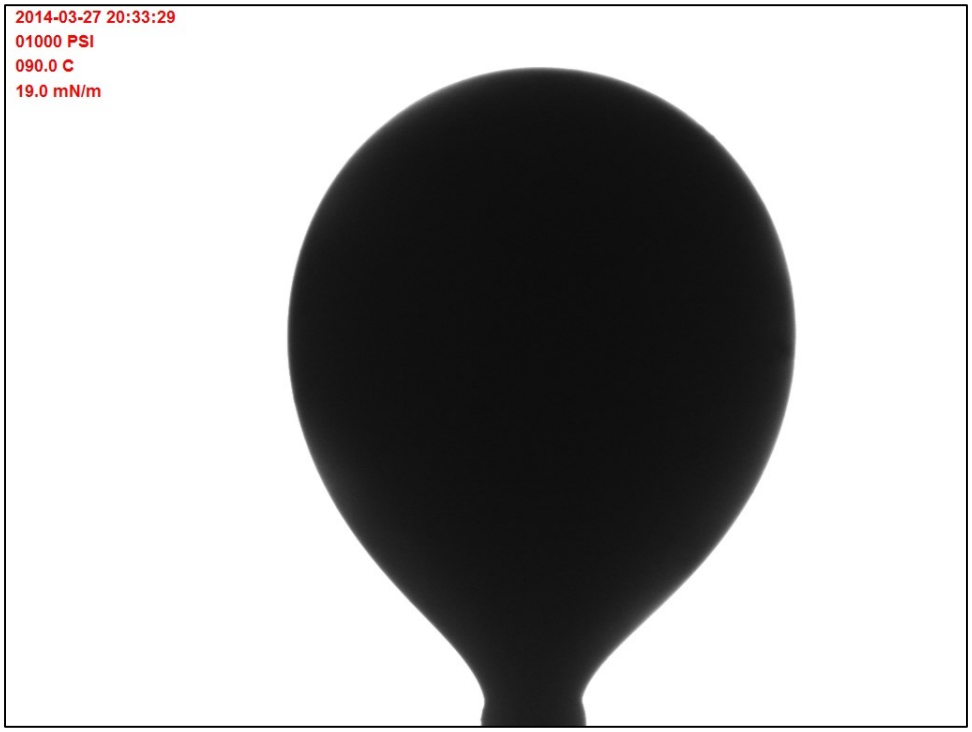


Figure 5.27: Shape of oil drop in sea water at 1000 psi

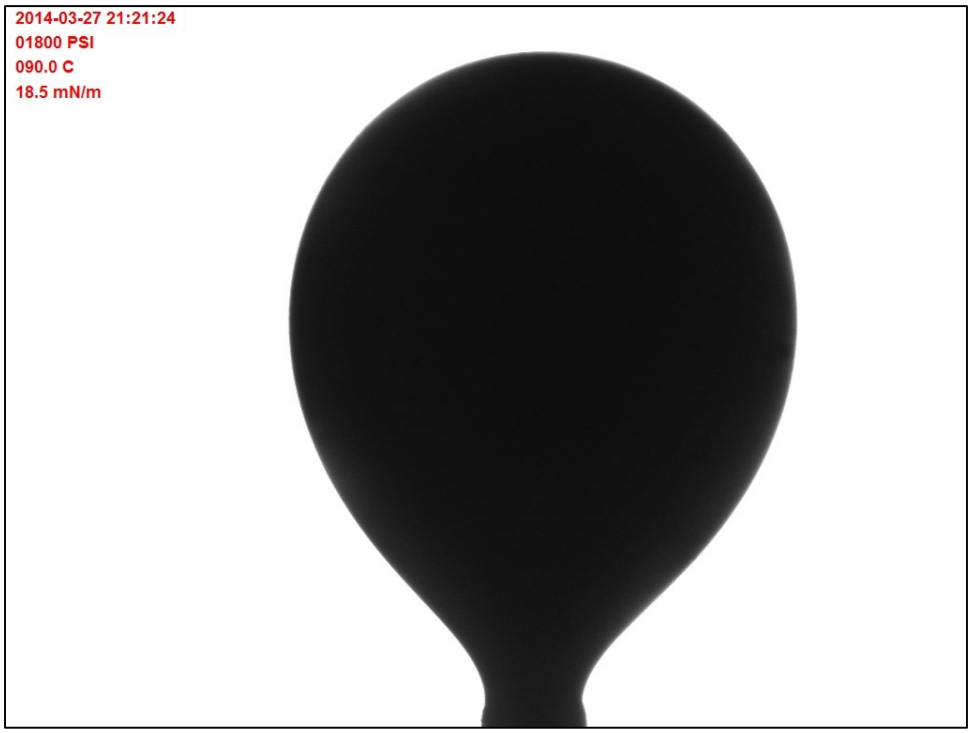


Figure 5.28: Shape of oil drop in sea water at 1800 psi

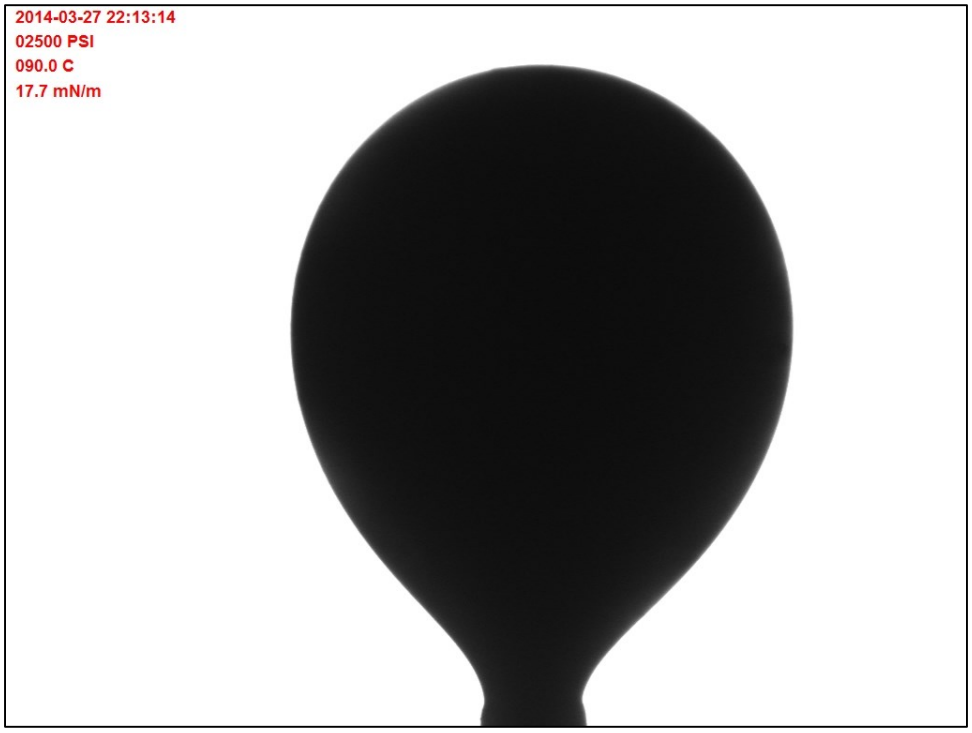


Figure 5.29: Shape of oil drop in sea water at 2500 psi

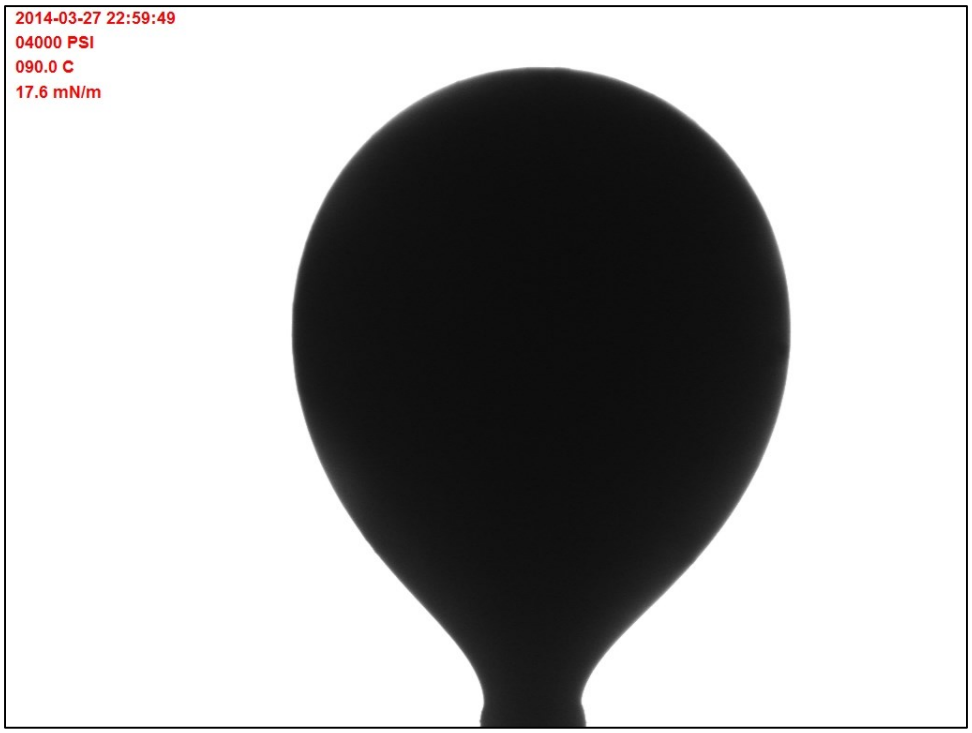


Figure 5.30: Shape of oil drop in sea water at 4000 psi

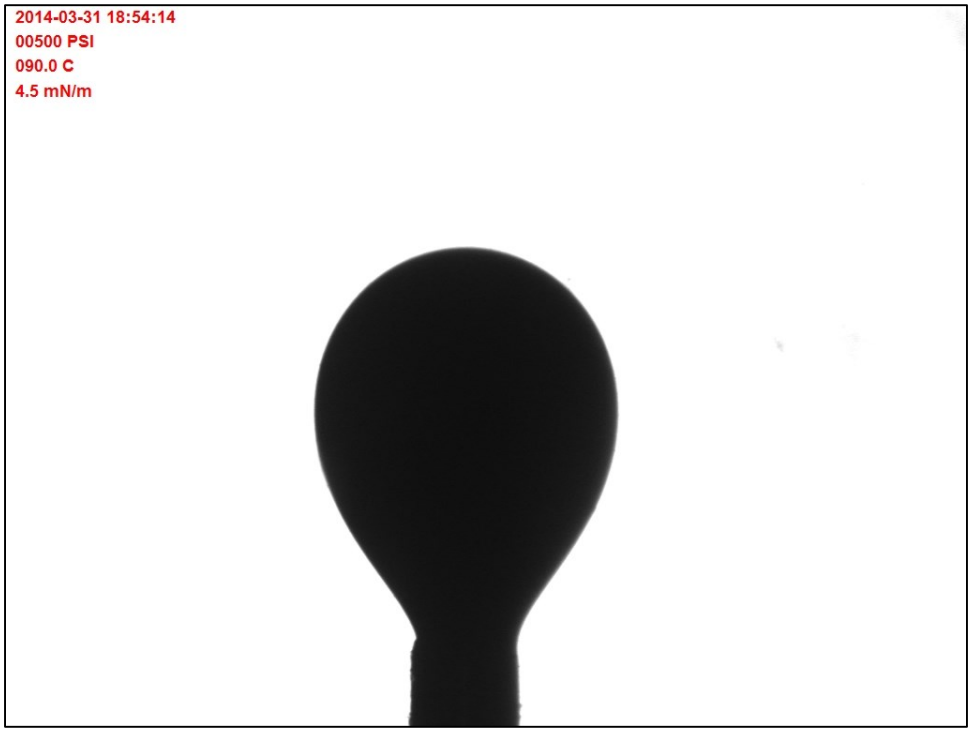


Figure 5.31: Shape of oil drop in surfactant solution at 500 psi

Figure 5.32: Shape of oil drop in surfactant solution at 1000 psi

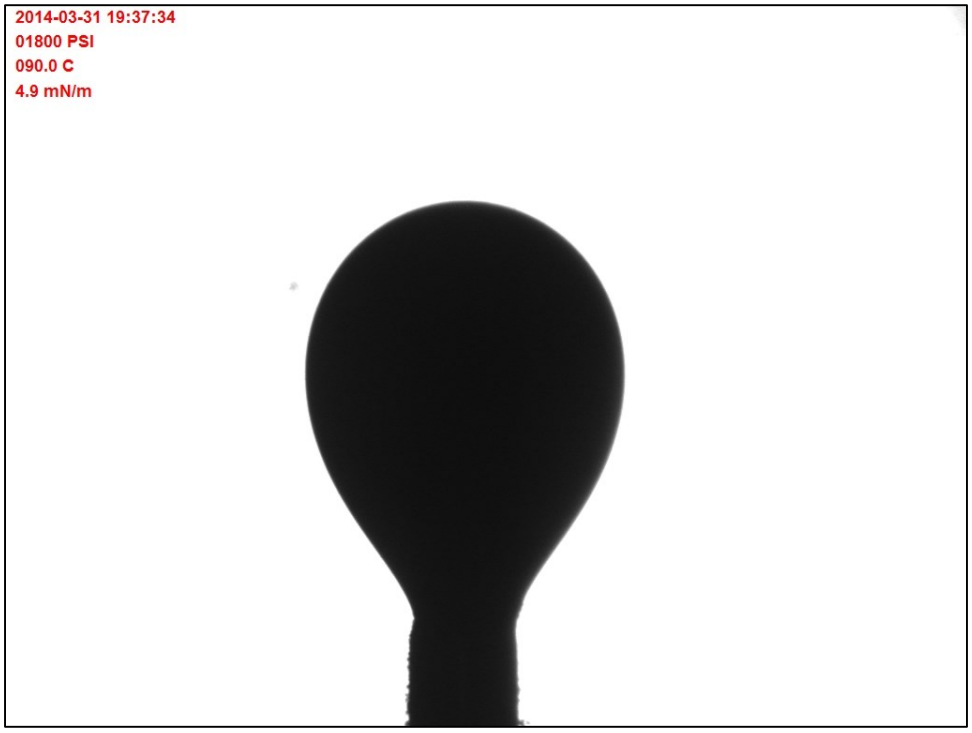


Figure 5.33: Shape of oil drop in surfactant solution at 1800 psi

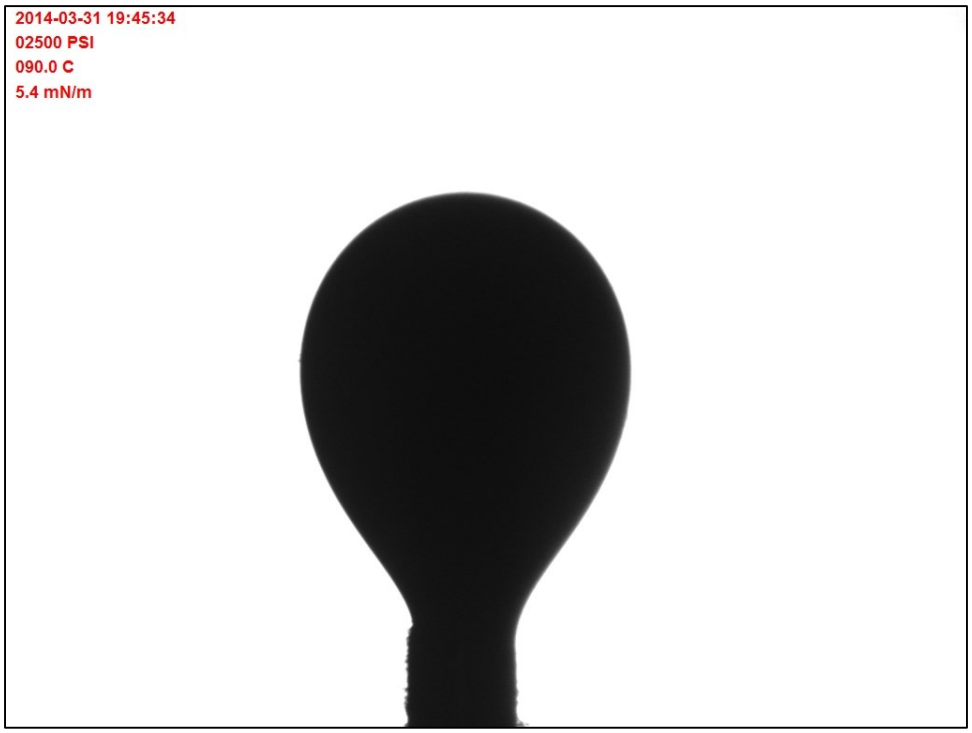


Figure 5.34: Shape of oil drop in surfactant solution at 2500 psi

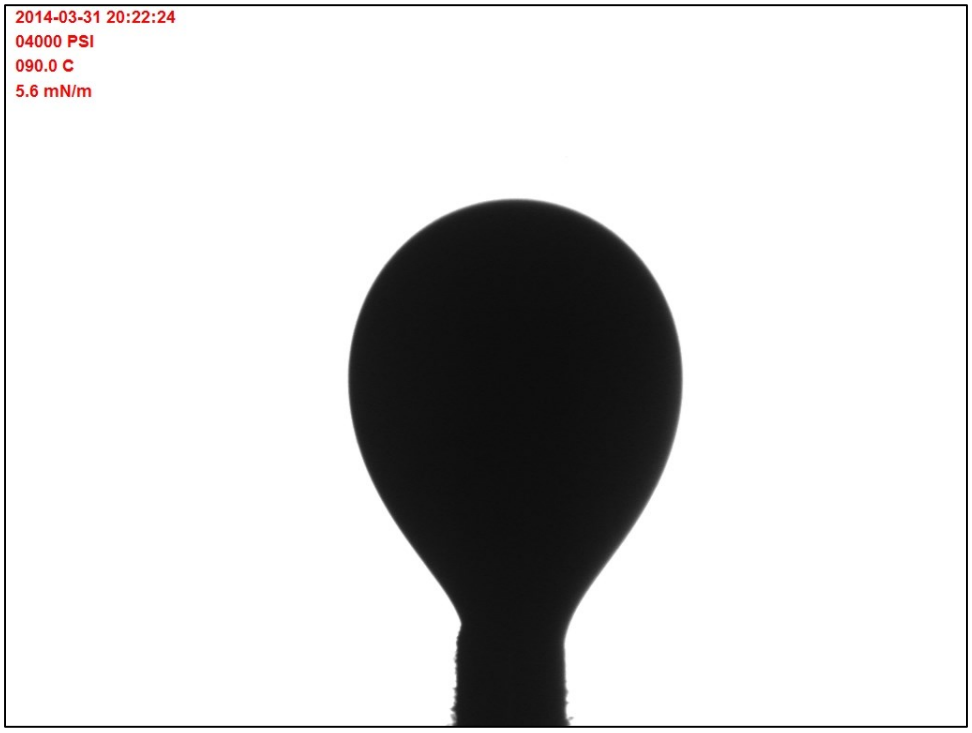
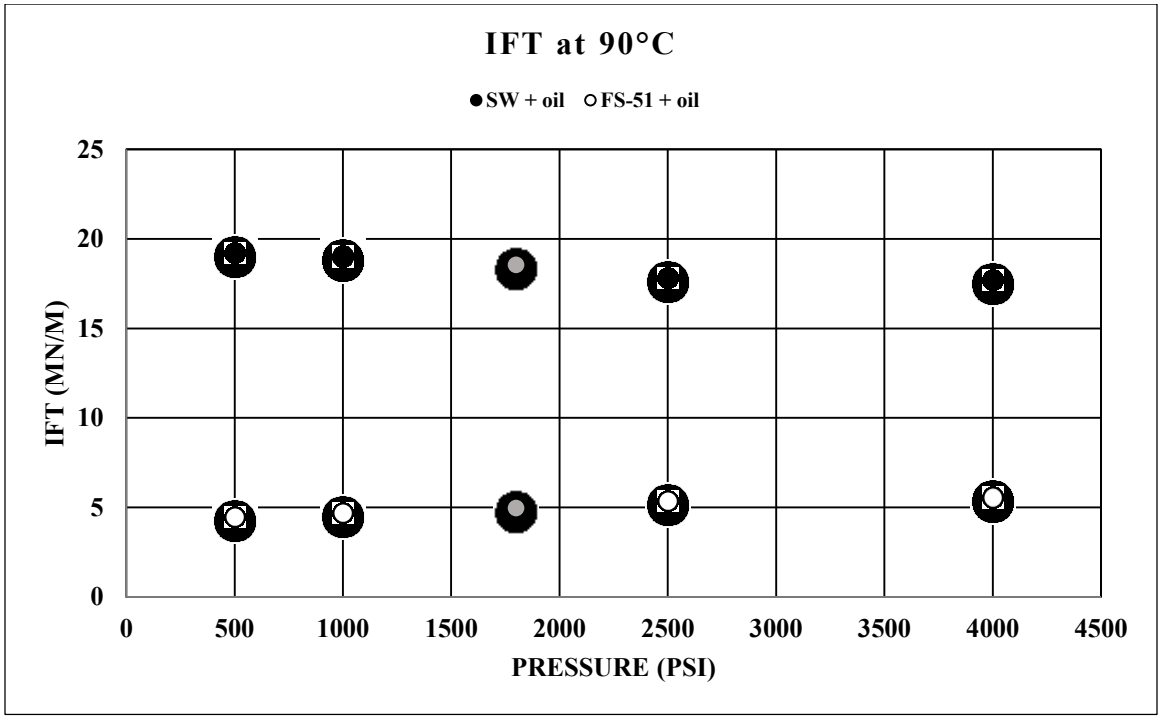


Figure 5.35 Shape of oil drop in surfactant solution at 4000 psi



- **Grey point indicates our core-flooding experiment condition**

Figure 5.36: IFT trends of the two systems at 90°C

5.4 Discussion of IFT Results

5.4.1 Surfactant Contribution in IFT Reduction

Regardless of the pressure drop across the core and the generation of foam, the increase in oil recovery during the surfactant solution injection was evident in all the experiments. This may be due to the reduction in interfacial tension caused by the presence of surfactant [22] [45] which reduces the capillary forces making the oil movable. To ascertain this phenomena, IFT tests were conducted at high temperature and pressure, including the condition at which the core-flooding experiments were performed. IFT measurements were done firstly between the injected brine (sea-water) and the dead oil used in the core-flooding and secondly between the surfactant solution and the dead oil. The surfactant solution was made using the fluoro-surfactant with 0.15% (vol.) concentration in the injection brine (sea water). This was the same surfactant solution that was used in the earlier core-flooding experiments. Results showed that there was significant reduction in the IFT due to the addition of the fluoro-surfactant even at this very low concentration. This also established the fact that this surfactant is stable at high temperature and high salinity.

5.4.2 Effect of Pressure on IFT

The effect of pressure on the IFT measurements was evident in the values obtained. As the pressure increased, the IFT values increased slightly for the surfactant solution and oil combination. This shows that at higher pressures, the surfactant performance decreases slightly and the highest value of the IFT (5.56 mN/m) for this combination was obtained at the highest measured pressure (4000 psi). The increase in IFT meant that the drop was more stable and this was evident as the drop diameter and volume increased slightly with

increase in pressure. The values of the drop diameter with pressure for the fluorosurfactant-oil combination are tabulated in Table 5.15 and plotted in Figure 5.37.

Table 5.15: Drop diameter of oil in surfactant solution during IFT measurements

Fluoro + oil	
Pressure (psi)	**Drop diameter (mm)**
500	1.81
1000	1.87
1800	1.91
2500	1.97
4000	2

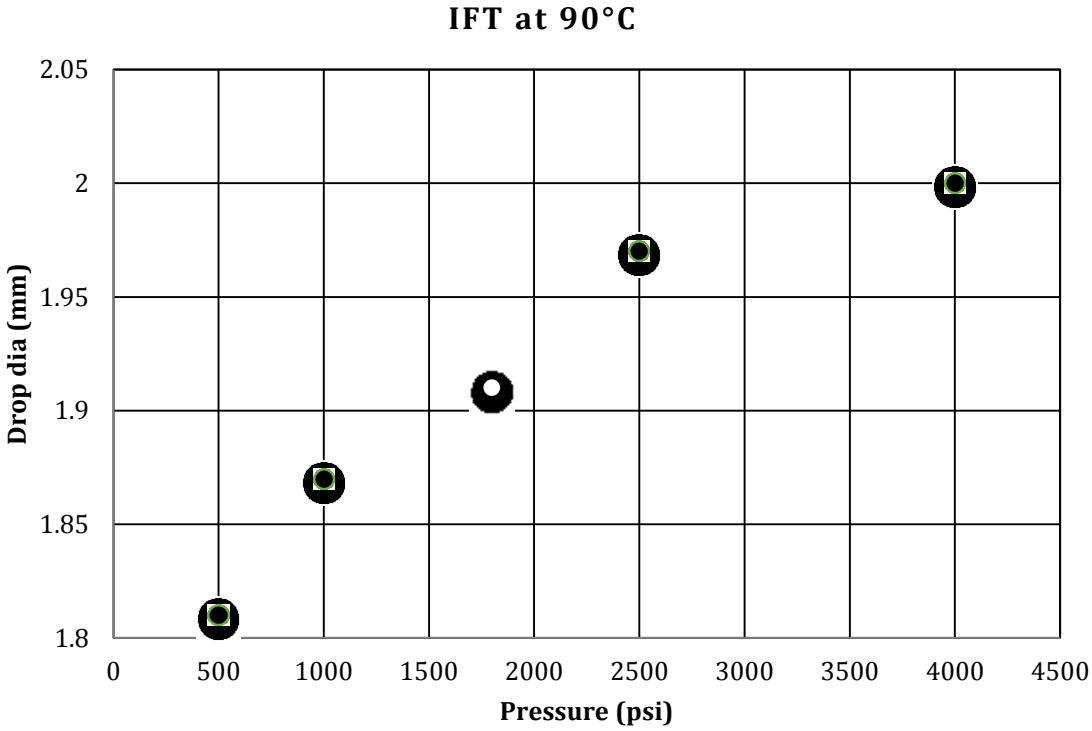


Figure 5.37: Drop diameter of oil in the surfactant solution during IFT measurements at 90°C, with white point indicates our core-flooding experiment condition

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

This research was conducted as part of an ongoing and continuous effort at the Center of Petroleum and Minerals at the Research Institute of KFUPM to come with the best EOR practice for different conditions. A number of EOR projects are being planned and executed in parallel at the Center to achieve this goal. This study will provide a significant addition and a step forward in the attainment of the overall objective. Furthermore, it will add to the Carbon Capture and Sequestration (CCS) study also being conducted at the Center, as it gives a viable option of CO_2 storage in addition for EOR.

The research started with the complex modification of an existing setup to develop a core-flooding system that was suitable for the experiments planned. All the coreflooding experiments were performed on this system and the results from these experiments and the IFT tests as discussed in chapter 5, lead us to the following conclusions:

1. The surfactant-CO_2 system proved quite effective for incremental oil recovery, irrespective of the injection strategy or the formation of foam.
2. CO_2 was the main contributor to the increment, while surfactant delayed the breakthrough of gas.
3. A longer surfactant slug followed by short CO_2 slug led to much faster oil recovery.

4. The increment due to this system was evident even when the secondary recovery through brine flooding was low.
5. Continuous surfactant-CO_2 flooding indicated foam generation by the pressure drop response.
6. The fluoro-surfactant performed better than the other surfactant, both in terms of oil recovery and the pressure drop response.
7. The contribution of the fluoro-surfactant in the oil recovery was confirmed by IFT tests, which showed significant decrease even at the low concentration of the fluoro-surfactant used. This test also showed the stability of the fluoro-surfactant at high temperature and high salinity.

Based on the observations and conclusions of this research, the following recommendations are suggested for future work in this area.

1. Visual foam tests should be conducted at the reservoir conditions using different surfactants and the effect of salinity, temperature and presence of oil studied, to come up with a stable foam system capable of withstanding these conditions.
2. This system should then be applied to core-flooding experiment to see the increment of oil recovery by foam, as the subject of foam generation and propagation inside the reservoir still remains an ambiguous subject.
3. Adsorption tests should be performed at the desired conditions between the selected surfactant and the rock. Adsorption reduces the effectiveness of the surfactant and this issue should be addressed in future studies.

4. IFT experiments should be done using different concentrations of surfactant with multiple surfactants and at variable salinities. These experiments will supplement the core-flooding results.

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